



Santé et Bien-être social Canada Health and Welfare Canada

354.0 75U

# survey and test protocols for point-of-use water purifiers



254.0 1464 7754 KD 3290

# SURVEY AND TEST PROTOCOLS FOR POINT-OF-USE WATER PURIFIERS

### ENVIRONMENTAL HEALTH DIRECTORATE HEALTH PROTECTION BRANCH

fersonalizzati Bofescaza (Balty for Doministicy Vialor Supply

AUGUST 1977

77-EHD-8

### COPIES OF THIS REPORT CAN BE OBTAINED FROM:

INFORMATION SERVICES, DEPARTMENT OF NATIONAL HEALTH AND WELFARE, BROOKE CLAXTON BUILDING OTTAWA KIA 0K9

#### THIS DOCUMENT WAS PREPARED UNDER CONTRACT BY:

"THE ONTARIO RESEARCH FOUNDATION"

JULY 1977

D.K. SMITH G.H. THOMAS J. CHRISTISON E. CHATFIELD

THE REPORT IS REPRODUCED AS RECEIVED FROM THE CONTRACTOR. THE CONCLUSIONS AND RECOMMENDATIONS CONTAINED HEREIN REPRESENTS THE OPINION OF THE CONTRACTOR AND DO NOT NECESSARILY CONSTITUTE ENDORSEMENT BY THE DEPARTMENT OF NATIONAL HEALTH AND WELFARE.

# TABLE OF CONTENTS

### SUMMARY RÉSUMÉ

1.0	INTR	ODUCTION	1
2.0	CHLO	RINE - Introduction	8
	2.1	Chlorine residual, time relationship for super-	8
	2.2	Chlorination equipment	10
	2.3	Limitations, problems in superchlorination practice	11
	2.4	Biological criteria for evaluation	13
	2.5	Manufacturers/suppliers of chlorination equipment	14
	2.6	References, superchlorination	16
		Figures 1, 2	17
3.0	IODII	NE - Introduction	18
	3.1	Methods of Iodinating water	18
	3.2	Determination of Iodine residuals	19
	3.3	Biological criteria for evaluation	20
	3.4	Iodine releasing resin type unit	20
	3.5	Physiological effects of the long term ingestion of iodine	21
	3.6	Manufacturers/suppliers of iodine equipment	22
	3.7	References - Iodine	23
		Figures 1 - 4	24

4.0	OZON	E - Introduction	26
	4.1	Generation of Ozone and Biocidal Properties ,,,,,,,,	26
·	4.2	Determination of Ozone residuals	28
	4.3	Ozone Water Purifiers for the home	28
	4.4	Criteria for evaluation	29
	4.5	Manufacturers/suppliers of ozone equipment	31
	4.6	References - Ozone	32
		Figures 1 - 2	33
		Proposed Ozone Standard Specifications (IOI)	34
5.0	ULTRAVIOLET WATER PURIFIERS - Introduction		
	5.1	Sources of U.V. and their characteristics	37
	5.2	Measurement of dosage - Physical detectors and biological detectors	38
	5.3	Interferences	41
	5.4	Criteria for Acceptability of a U.V. unit	41
	5.5	Types of commercially available U.V. units ,,,,,,,,,	42
	5.6	Biological criteria for evaluation	45
	5.7	Recommendations ,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	46
	5.8	Manufacturers/suppliers of U.V. equipment ,,,,,,,,	47
	5.9	References - Ultraviolet	49
		Policy Statement by United States Public Health Service on use of UV for Disinfection of Water	50
6.0	SILV	ER - Introduction	52
	6.1	Interferences	52
	6.2	Water Purifiers using Silver (Bactericidal & Bacterio- static)	53
		* * * * * * * * * * * * * * * * * * * *	

	6.3	Bactericidal silver units	54
	6.4	Criteria for evaluation of silver units	56
	6.5	Suggested test protocol for evaluating bactericidal	00
		silver units	58
	6.6	Information obtainable from suggested test protocol	61
	6.7	Discussion on neutralization of silver	62
	6.8	Manufacturers/suppliers of bactericidal silver units	64
	6.9	References - silver	65
		Figure 1 - Test manifold design	66
7.0	BACTI Intro	ERIOSTATIC FILTERS (SILVER/ACTIVATED CARBON)-	67
	7.1	Bacteriostatic or bacterial reduction claims	67
	7.2	Suggested test protocol for bacteriostatic silver/ carbon units	69
	7.3	Manufacturers/suppliers of Bacteriostatic type filters	74
8.0	DIST	ILLATION TYPE WATER PURIFIERS - Introduction	76
	8.1	Distillation units	76
	8.2	Limitations and potential problems	76
	8.3	Test protocol for efficiency of removal of organics	77
	8.4	Manufacturers/suppliers of small distillation units	78
9.0	REVE Int	RSE OSMOSIS, ULTRAFILTRATION UNITS -	79
	9.1	Factors affecting R.O. performance	80
	9.2	Claims for R.O. systems	81
	9.3	Test protocol for particulate, inorganic and organic removal claims	81

	9.4	Tests for bacterial control	82
	9.5	Manufacturers/suppliers of small RO units	83
10.0	ACTI	VATED CARBON - Introduction	84
	10.1	Activated carbon filter units	85
	10.2	Test protocol for evaluation of carbon filters	87
	10.3	Manufacturers/suppliers of activated carbon units	88
	10.4	References - activated carbon	89
11.0	FILT	RATION UNITS - MISCELLANEOUS	90
	11.1	Commandment Industrial Limited KS22	90
	11.2	Rohm & Haas Ambersorb XE342 and XE352	91
	11.3	Manufacturers/suppliers of miscellaneous filters	92
	11.4	References - filtration units	92
12.0	ORGA	NICS REMOVAL ,	93
	12.1	Introduction	94
	12.2	Outline of test protocol	95
	12.3	Analyses	96
	12.4	Addendum - experimental tests	99
	12.5	References - organics removal	101
13.0	TRAC	E METALS - Introduction	102
	13.1	Recommended test protocol for trace metals	109
	13.2	Other Recommendations	110
	13.3	Addendum	112
	13.4	References - trace metals	113

·

ł

:

		Table I
		Figures I, II
14.0	ASBE	STOS FIBRE REMOVAL - Summary
	14.1	Recommended test specifications
	14.2	Introduction
	14.3	Experimental
	14.4	Statistical treatment of results
	14.5	Results of experimental tests on four filter units129
	14.6	Conclusions ,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,
	14.7	References - Asbestos
		Figures 1 to 5
		Table I and Table 2
15.0	PART THAN	ICULATE REMOVAL CLAIMS AND TEST PROTOCOLS (OTHER ASBESTOS)138
	ACKN	OWLEDGEMENTS

#### SUMMARY

A number of different water treatment methods for pointof-use disinfection and treatment of raw water for domestic consumption are reviewed. These include systems based on chlorine, iodine, ozone, ultraviolet, silver and distillation. In addition, treatment systems, such as reverse osmosis units and activated carbon/silver units, designed to be used on a potable water supply for taste, odour, particulates, inorganic and organic dissolved solids, reduction or removal have been reviewed. Documentation of the various methods of treatment is presented together with limitations and potential or real problems which may arise in practice. Recommendations for further investigation in areas in which information is inadequate or where a problem may exist have been made. Criteria and/or test protocols for evaluating claims made by manufacturers on the ability of their products to reduce or remove various contaminants from water have been suggested.

#### RÉSUMÉ

Plusieurs méthodes de désinfection de l'eau au point d'utilisation et de traitement de l'eau brute pour consommation domestique sont examinées, y compris des systèmes fondés sur l'utilisation de chlore, d'iode, d'ozone, de lumière ultraviolette, d'argent et également de la distillation. Ont été en outre examinés des modes de traitement faisant appel à l'utilisation d'unités à osmose inverse et d'unités carbone/ argent, conçus pour le traitement des approvisionnements en eau potable, en ce qui concerne la diminution ou l'élimination du goût, de l'odeur, des particules et des solides inorganiques et organiques en solution. De la documentation sur les diverses méthodes de traitement est présentée, et on traite en même temps des limites et des problèmes éventuels ou des problèmes réels qui peuvent surgir dans la pratique. Des recommandations relatives à des études plus poussées dans des domaines pour lesquels la documentation est inadéquate ou dans lesquels il existe un problème ont été formulées. On a également proposé des critères et/ou des protocoles d'essais visant l'évaluation des allégations des fabricants selon lesquelles leurs produits sont efficaces en ce qui regarde la diminution ou l'élimination de divers contaminants dans l'eau.

#### INTRODUCTION

Recent emphasis on the quality of drinking water by the news media and government agencies has resulted in a variety of point-of-use water purifiers intended primarily for domestic use appearing on the market. The sale of these water purifying devices has, in a number of instances, been accompanied by promotional literature containing unsubstantiated or poorly substantiated claims. One of the more imaginative and amusing claims encountered was one in which a silver/activated carbon device was said, in the case of water shortage or emergency, to purify the water contained in a water bed for drinking purposes! Unfortunately, reputable manufacturers with modest claims which can be substantiated are likely to be placed at a marketing disadvantage when in competition with manufacturers making sweeping claims for their products. Many companies have entered the field in the last two to three years and just as rapidly have disappeared, merged or re-appeared under a new name. As a result it is difficult to keep an up-to-date list of manufacturers, units available and claims made.

Government health and regulatory agencies in the United States and Canada have been concerned about the claims made and efficacy of some of these devices, and have recently focussed attention on the problem. In Canada the Health Protection Branch of the Department of National Health and Welfare, Ottawa commissioned the present study, and the Ministry of Health, Ontario has formed an ad hoc committee on "Home Water Purifiers." In the U.S.A. the Environmental Protection Agency (EPA) in June 1975 published interim criteria standards for use in evaluating applications for registration of water purifiers under the Federal Insecticide, Fungicide and Rodenticide Act. These interim standards were intended principally for the evaluation of bactericidal claims of water purifying devices using silver as an antimicrobial agent. In August 1976 evaluation criteria were extended by EPA to cover silver/carbon water filters which are intended for home use for the removal of chemicals, odors, and color from potable municipal water.

In addition to governmental regulations and criteria for evaluation of water treatment devices, the industry has formed a group known as the Water Quality Improvement Standards and Certification Council (WQISCC) under the aegis of the Water Quality Association in the U.S.A. One of the functions of WQISCC is to draft test protocols and standards to be used for certification of water treatment devices. At the present time it is expected that the fifth, and possibly final, draft of proposed test protocols and voluntary standards for portable, household and commercial units for treating water for human consumption will be available in September 1977.

Point-of-use home water "purifiers" fall into one or more of several general categories depending on their construction and upon the claims made for their use. The following three categories have been suggested by the Water Quality Improvement Standards and Certification Council (WQISCC) in the U.S.A. in their proposed interim voluntary standards for portable, household and commercial units for treating water for human consumption.

#### Microbiological treatment

These products are designed to ensure a microbiologically safe water for drinking. If used in the treatment of raw water or water of unknown bacteriological quality, such products must be bactericidal. If they are intended for the further treatment of a water which is already considered microbiologically safe, such as a municipal supply, they may be only bacteriostatic, i.e. prevent bacterial growth; or accomplish some bacterial reduction.

#### Chemical removal devices

These products are designed to remove one or more specified organic or inorganic constituents from water. Chemical removal devices

- 2 -

may fall into several different classifications, e.g. distillation units, carbon adsorption, ion exchange, reverse osmosis etc. but are more conveniently classified by the type of contaminant removed rather than the method of removal.

#### Particulate removal

These are devices intended to remove by mechanical means particulate matter from water, such as asbestos, organic and inorganic solids, cysts, spores, bacteria.

Many units, because they are designed as water treatment systems, may fulfil more than one function. For example, a purifier using a ceramic filter together with silver and activated carbon, may be able to claim efficacy in all three categories, in which case each of the major functions can be tested and evaluated under the headings of (1) microbiological, (2) chemical and (3) particulate.

#### Microbiological Treatment (Disinfection)

A basic tenet in water treatment is the removal or destruction of disease-producing biological agents so that any unit designed to treat raw water or water of unknown microbiological quality must have this capability. In municipal practice, water treatment usually involves storage, settling, chemical flocculation, filtration and disinfection. Home water purifiers to treat spring, well, lake or river water of unknown microbiological quality must at least disinfect the raw water supply. If proper care and application of one of the many disinfection procedures available is taken, a water that contains no demonstrable pathogenic microorganisms will result. Because of the importance of disinfection, emphasis, initially, in this report will be placed on that aspect. Chemical removal and particulate removal from water will also

- 3 -

be dealt with to some extent during discussion of disinfection processes since limitations and/or interferences are often placed on the disinfection method by the presence of chemicals and particulates. Test protocols or criteria for evaluation (if no test protocol is deemed necessary) of the water treatment unit will also be primarily related to disinfection.

No matter what disinfecting agent is used to treat water, reliable techniques for measuring the adequacy of treatment are required. In some instances, such as in the disinfection of water with halogens, measurement of the presence or absence of disinfectant residual after a specified contact time can be used, but with methods using ultraviolet light, ozone and silver this is difficult or impossible. Where residuals cannot be measured (or do not give a reliable indication of efficacy of disinfection) biological measurements are often used. The generally accepted biological measurement to determine the adequacy of water disinfection is to test for organisms of the coliform group. The rationale of the coliform group as indicator organisms of pollution may be found in "Standard Methods for the Examination of Water and Wastewater" 14th Ed. 1976. It is questionable as to whether the true biological safety of water can be adequately measured by coliform reduction if the resistance of viruses and cysts to disinfection processes is considered. This is particularly true for home water purification units where the benefits of storage, settling, coagulation and filtration of water are largely absent.

With modern water treatment technology a high quality drinking water can be produced from heavily polluted raw water sources. However, recommendations on the type of treatment required may be based on coliform numbers in the raw water.

In general, where total coliform densities exceed 1,000/100 ml in 10% of samples in any consecutive 30 day period then complete treatment (i.e. flocculation-coagulation, sedimentation, filtration and disinfection) is recommended. Where total coliforms exceed 5,000/100 ml in more than 10%

- 4 -

of samples auxiliary treatment using prechlorination is recommended, followed by complete treatment.

Where 10% of the raw water samples in any 30 day period have a total coliform density between 100 and 1,000/100 ml, a combination of flocculation-coagulation, sedimentation and filtration, followed by disinfection, is recommended. Any combination of these processes (partial treatment) may be employed but always including disinfection.

Where raw water samples contain any faecal coliform organisms or if more than 5% of samples in any consecutive 30 day period have a total coliform density greater than 10/100 ml, disinfection is required.

Home water purifying units rarely employ more than filtration and disinfection and as a result they are not suitable for heavily polluted waters where complete treatment is required.

No standards exist at the present time for viruses in water supplies although it is known that water contaminated with faecal wastes may also contain enteroviruses such as ECHO, polio and Coxsackie viruses A and B. In addition, other viruses such as infectious hepatitis and adeno and reoviruses may also be present in sewage contaminated water. It would, therefore, be highly desirable to have some evidence of virucidal activity by the disinfecting agent employed in a home type water purifier under conditions of use where the raw water is of doubtful bacteriological quality. It would also appear desirable for the disinfectant to have either cysticidal activity, or for the home water treatment system to employ a filtration unit which could retain cysts and protozoa such as E. histolytica and Giardia lamblia when treating raw water. As far as viruses are concerned, the American Public Health Association (APHA) held an international conference in Mexico City in 1974 to discuss detection and control of waterborne viruses. A number of recommendations were made by APHA, one of which was the need for the development of quantitative methodology for the recovery of small numbers of viruses from large volumes of water. They also suggested the establishment of standards for viruses in water of less than one virus in 380-3,800 l (100-1,000 gal US) of drinking water. Although various techniques are

- 5 -

available for concentrating viruses from water, all have limitations. Recently Fenters and Reed (1) and the Canadian Public Health Association (2) have summarized the advantages and disadvantages of the various methods for delineating the presence of viruses in water. One commercially available virus concentration device, the Aquella Wirus Concentrator (Carborundum Company) is said to be capable of isolating a single virus from as much as 100 gallons of water, and therefore approaches the detection limits required for the proposed APHA standard. Although desirable, it would be premature to try to establish test protocols for evaluating domestic water purifiers for virus removal or inactivation until virological surveys of drinking water supplies have been carried out and standards established.

#### Determination of efficacy of Chemical Removal claims

Where home water treatment devices are designed to remove one or more specified dissolved organic or inorganic compounds or ions from water, the chemical removal functions should be substantiated by tests similar to those suggested in the sections on organic and inorganic test protocols in this report. No test protocols for establishing general taste and odour removal claims have been given in this report.

#### Determination of efficacy of Particulate Removal claims

Where claims are made for the mechanical removal of particulate matter from water such as asbestos, spores, cysts, organic and inorganic solids, the functions claimed should be substantiated by tests similar to those outlined in the section on particulate removal in this report.

ì.

#### Categories of water treatment systems considered

The following methods or, rather, systems of disinfecting a raw water for home use will be considered in turn, reviewing (a) background and documentation on the method, (b) limitations, problems of the system in practice, (c) criteria and/or test protocol for evaluation of efficacy, (d) manufacturers and agents supplying the particular treatment units\* and (e) potential or real problems arising from method of construction or recommended application of a particular manufacturer's unit based on documentation in (a), (b) and (c):

- (1) Chlorine
- (2) Iodine
- (3) Ozone
- (4) Ultraviolet
- (5) Silver impregnated or silver/carbon filters
- (6) Distillation.

Other units which will be considered are reverse osmosis units for total dissolved solids removal, activated carbon and silver/carbon units designed for <u>potable</u> water use for taste, odour and organics removal. The silver/carbon units in this application need only be bacteriostatic or control the growth of microorganisms which may proliferate in the carbon bed.

#### Introduction References

- Fenters, J.D. and Reed, Josephine M. "Viruses in Water Supply" J. AWWA <u>69</u>, 328, 1977.
- 2. "Microbiological Quality of Drinking Water". Environmental Health Directorate, Health Protection Branch, Health and Welfare Canada, January, 1977. (Document prepared under contract by the Canadian Public Health Association).
- \* Every effort was made to ensure that the lists of manufacturers and/or suppliers were as complete as possible. The authors apologise for any errors or omissions made.

.

CHLORINE

. .

.

.

#### CHLORINE

#### Introduction

The disinfection of public water supplies with relatively low chlorine concentrations and long holding times has been accepted for many years. The relationship of chlorine concentrations, equilibria, temperature and pH, interferences and rate of disinfection have been thoroughly studied and put into practice.

In the case of small private water supplies it is difficult to obtain long holding times and also to obtain accurate dosing and monitoring of chlorine residuals, particularly where there are rapid changes in the quality of the water. As a result, the practice of superchlorination with comparatively high concentrations of chlorine, followed by a short contact time and removal of chlorine residual in a dechlorination step, usually by activated carbon, has become popular.

#### 2.1 Chlorine residual, time relationship for superchlorination

Varma and Bauman (1) in 1959 studied the available literature and reviewed the chlorine residuals and contact times required to kill (a) vegetative bacteria, (b) viruses and (c) amoebic cysts. This study led to the recommendation by Bauman (2) that under the adverse conditions of 0°C and a pH of 8.5, small water supplies should be superchlorinated with free available chlorine residuals of 5 to 6 mg/l for a contact time of 7 minutes. Adoption of this recommendation would provide bactericidal and virucidal dosages. Cysts (<u>Endamoeba histolytica</u>) which would survive this treatment could be removed on precoat carbon filters which would be used for removal of excess chlorine after the requisite contact time. This was thought to be a "worst case" water since most well or pond water sources do not approach a temperature of 0°C and a pH of 8.5. A number of other recommendations for different residual and contact times at higher temperatures and lower pH were also advanced. Bauman

2.0

and Ludwig (3) finally standardized on Coxsackie virus as the upper limit of resistant pathogens to be destroyed. They prepared a series of time, temperature and free residual chlorine correlation envelopes with the general equation

> C<sup>n</sup>t = K where C is the concentration of free available chlorine residual,

- n is a positive number expressing the relationship between C and t, and
- K is a constant for a given organism (in this case Coxsackie virus), water pH and water temperature.

Suppliers of superchlorination equipment have standardized their superchlorination practices on the basis of graphs or tables of disinfection versus free available chlorine residuals (Figure 2) with a Ct = 20 or Ct = 30. One major Canadian supplier (Everpure) uses a design figure of Ct = 30 with a normally recommended contact time of 10 minutes at  $\sim$ 3 mg/l free available chlorine residual. Other time/FAC residuals may also be selected from the graph (e.g. 6 minutes at 5 mg/l at a Ct = 30) to allow for different desired flow rates and contact times.

It should be noted that by selecting Coxsackie virus as the upper limit of resistant pathogens to be destroyed for the preparation of these time/FAC residuals, pathogenic vegetative bacteria and polio virus are also destroyed. More resistant organisms such as amoebic cysts are not destroyed, but removal of these can be carried out by filtration. It is uncertain as to whether high levels of inactivation of hepatitis virus are achieved when using Coxsackie virus as the upper limit for disinfection of small water supplies. Nevertheless, a considerable margin of safety is assured with regard to enteric bacterial diseases with good superchlorination practices.

- 9 -

#### 2.2 Chlorination equipment

Basic equipment required for superchlorination/dechlorination of water supplies consists of (a) a chemical feed pump suitable for pumping chlorine solutions, (b) hypochlorite (bleach) supply reservoir, (c) a well pump (usually a jet pump) and (d) pressure tank which also serves as a chlorine contact tank, (e) a dechlorinating filter with provision for backwash. A typical installation is shown in Figure 1. Note that the chlorine feed pump is wired to run when the well pump comes on and that chlorine is injected into the water line between the well pump and the pressure tank.

An added benefit of superchlorination/dechlorination systems is that in addition to bactericidal problems a number of water quality problems associated with small water supplies can be overcome with very little extra equipment. According to USPHS Manual #24 dealing with Individual Water Supplies "iron and manganese can be removed by a combination of automatic chlorination and fine filtration. The chlorine oxidizes the iron, kills iron bacteria, and eliminates any disease bacteria that may be present. The fine filter then removes the precipitated iron (provided the pH is above 6.8). Some filters may dechlorinate also. This chlorination-filtration method provides complete correction of the iron problem and assures disinfection as well."

Other problems which can be corrected at the same time using superchlorination/dechlorination systems are acid waters by feeding soda ash along with the hypochlorite. Hydrogen sulphide can be oxidized in sulphide containing waters by adjusting the hypochlorite dosage to satisfy the sulphide demand and provide a free residual.

#### 2.3 Limitations, problems in superchlorination practice

Although the equipment required is fairly simple, a thorough understanding of the principles of superchlorination/dechlorination and information on the water supply to be treated are necessary if a well engineered and operating system is to be installed. Where superchlorination/dechlorination systems are sold as a packaged water supply system by the manufacturer it is easier to ensure proper operation. Maximum flow is known and can be regulated, and the pressure tank/chlorine contact tank can be adequately sized for correct retention time. Adjustment of the chlorine feed pump to the actual water pumping rate and the chlorine demand of the particular supply must be made. This entails setting up the chlorinator to give a 3 to 5 mg/1 residual after two or three minutes contact. Attempts to "retrofit" existing well pumps and pressure tanks with a chlorinating feed pump and supply reservoir are likely to lead to erratic and uncertain chlorination practices. The usual pressure tank in such situations is of 5 to 40 gallon total capacity. Only about 50% of the volume may be liquid capacity because of the appreciable air cushion. This is inadequate for superchlorination unless high free chlorine residuals are maintained (>5 mg/l). Even then, adequate mixing may be a problem. In some instances it is possible to chlorinate directly into the well casing to obtain the requisite contact time.

Reasonable design dictates a minimum of a 40 gal functional volume pressure tank ( $\sim$ 80 gal total) or separate chlorination mixing and contact tank and a free available chlorine residual of 3 to 5 mg/l. This would satisfy a Ct = 30 for a flow rate of  $\sim$ 4 gal/min at 3 mg/l FAC and  $\sim$ 6 gal/min at 5 mg/l.

Rugged corrosion resistant equipment and fail-safe features are highly desirable in a superchlorination system. The chemical feed pump must discharge into a pressurized system and therefore must be capable of withstanding starts under full load conditions. Check valves should be fitted to prevent back flow and also anti-siphon devices if there is suction on the water line. Precise feed-rate adjustment low volume chlorinating feed pumps are preferred since higher feed rate

- 11 -

pumps which require dilution of the hypochlorite supply with water can lead to precipitation problems, particularly with hard water. Most chemical feed pumps are of the diaphragm positive displacement type with inlet and outlet poppet valves. If precipitates, grit or other debris, get through the inlet screen or strainer and under the inlet valve, hypochlorite solution will not be pumped to the water supply on the power stroke. Most chemical pump problems can be attributed to the passage of solids through the valve system so that a good strainer is essential. Provision for a low level alarm system on the hypochlorite reservoir is highly desirable. The chlorinating system in a superchlorination/dechlorination system usually serves the total water supplied to the household but frequently only a dechlorinated supply is provided to a tap or taps in the kitchen for culinary and drinking purposes. It is important to ensure that the rate at which chlorinated water is drawn for non-consumptive purposes does not reduce the required retention time below the minimum required for disinfection of water used for drinking purposes. Dechlorination is normally carried out with activated carbon filters or with precoat carbon filters in the form of disposable cartridges for smaller installations. Larger installations usually employ granular bed filters of activated carbon with backwash provision.

Carbon filters are prone to become contaminated with bacteria after a period of time. This is one area which probably warrants further investigation since the organisms most likely to colonize the filter are spore formers which have not been killed by superchlorination. It is suggested that the numbers and types of bacteria, as well as any toxic products, be investigated. Toxic products (e.g. halomethanes) in the final product water could arise from chlorination of humic substances in water and metabolic products of bacteria growing on the filters. Although chlorinated hydrocarbons will be removed to some extent by activated carbon filters, eventual bleed-through is likely. At least one manufacturer (American Water Purification Inc.) has recognized the problem of growth on carbon beds after chlorination - with their Silverator  $^{(B)}$  pre-treatment system using silver booster (chlorine) + Silverator  $^{(B)}$  holding tank, followed by their Home Silverator  $^{(B)}$  filter containing Silverstat  $^{(B)}$ , a silver/activated carbon bed to remove residual chlorine.

#### 2.4 Biological criteria for evaluation

It is the opinion of the writer that challenge tests with indicator organisms such as coliforms are not required in superchlorination/dechlorination systems, provided it can be shown that the free available chlorine residual is in the range of 3 to 5 mg/l before dechlorination and that a contact time of 6 to 10 minutes is maintained at this recommended concentration of chlorine under maximum flow rate conditions in the system. These conditions will satisfy a Ct = 30 (Fig. 2) in water up to a pH of 8 and with a temperature of 5°C. Flow control devices must be fitted to ensure that adequate retention times are maintained. Poor mixing within the chlorine contact tank may cause problems and result in a lower retention time than is theoretically obtainable. This is most likely to be a problem in the design and installation of "retrofit" systems.

Proof of disinfection can be obtained from installed units in the field by having the treated water supply examined for coliforms by the Provincial health authority at intervals of about one month using the routine sample bottle method to collect a sample after the disinfection step. It is also recommended that a sample of the raw water supply before chlorination be examined at the same time to ensure that total coliforms are within guidelines (100-1,000/100 ml) suggested for treatment by simple disinfection and filtration procedures. 2.5 Manufacturers/Suppliers of Chlorination Equipment

> Everpure Division of Culligan of Canada Ltd. Sheridan Park Mississauga, Ontario L5K 1A5

AMF Cuno 52 Royal Road Guelph, Ontario N1H 6N1

Ecodyne Mec-O-Matic Company P.O. Box 2430 St. Paul, Minnesota 55165 Trade Name/Model

#### Systems

- Everpure Water Supply System

   packaged unit with PD-10 chlorine pump, jet water pump supply tank, pressure/contact tank and dechlorinator.
- (2) Everpure Water Purification System. Manual superchlorination/dechlorination system designed for Recreational Vehicles. Kit with QC2-AC filter.

#### <u>Chlorinators</u>

- Everclor Automatic Chemical feeder pumps Models PD-4, PD-10 and PD-20 for use with solution container, standard pressure tank and pumped water supply.
- Everclor Automatic Chemical feeder Models AC 7 and AC 22 as above.

Dechlorinating equipment - cartridge type

Everpure QC series e.g. QC4 water filter including activated carbon

Everpure T series, e.g. T4 and T20

Everpure C3 and C5

#### Chlorinators

Aqua-Pure Adjustable Chemical Chlorine Feeder, designed for use <u>after</u> normal pressure tank into a properly sized holding tank (typically 80 gal).

#### Dechlorinators

Aqua-Pure AP117, AP217, AP227 Cartridges in various housings.

#### Chlorinators

Various

Mec-O-Matic Models 475C for 5 gpm well pump rate to Model D60DI for 600 gpm well pump rate.

<u>Dechlorination</u> - no activated carbon filters listed in catalogue. Presumably commercially available carbon cartridges are used. Manufacturers/Suppliers

Trade Name/Model

System

American Water Purification Inc. 1990 Olivera Road Concord, California 94520 U.S.A.

Silverator pre-treatment system consisting of chlorine (Silverbooster), supply tank and tank, and Home Silverator R dechlorination filter of activated carbon/silver.

#### Superchlorination References

- 16 -

- Varma, M.M. and Bauman, E.R. "Superchlorination-Dechlorination of Small Water Supplies." Sta. Progress Report, Project 353-5 Iowa State University Eng. Experimental Section, Ames, Iowa. 1959
- Bauman, E.R. "Should Small Water Supplies be Superchlorinated?" Water & Sewage Works <u>108</u>, 463, 1961 and <u>109</u>, 21, 1962
- Bauman, E.Robert and Ludwig, David D. "Free available chlorine residuals for small non-public water supplies."
   J. AWWA, <u>54</u>, 1379, 1962.

2.6



- 17 -





IODINE

.

#### IODINE

Chang and Morris (1)(2) in 1953 demonstrated the effectiveness of iodine as a water disinfectant against bacteria, viruses and cysts. Their studies were largely responsible for the adoption of iodine by the military for the disinfection of water in the field, mainly in the form of globaline tablets(20 mg tetraglycine hydroperiodide with disodium dihydrogen pyrophosphate and talc). One tablet imparts about 8 mg/l I<sub>2</sub> to water and at this concentration will destroy cysts of <u>E. histolytica</u> and other bacterial and viral enteric pathogens in 10 minutes. Black and co-workers (3) in 1963 to 1965 conducted studies on the effectiveness of iodine for the disinfection of public water supplies and its physiologic effects on human beings. Two water systems disinfected with iodine serving some 700 people at three correctional institutions were studied and it appears that no harmful physiological effects to those consuming the water have resulted (4).

The disinfecting ability of iodine is not affected as much as chlorine by high pH or the presence of organic or other nitrogencontaining substances. Iodine will not, however, precipitate iron or manganese but will react with hydrogen sulfide. The oxidizing power as far as taste and odour removal is concerned is more limited than that of chlorine.

#### 3.1 Methods of Iodinating Water

There are several methods of application of iodine for the treatment of water. The simplest method is to meter a saturated aqueous solution of  $I_2$  into the water. This can be most readily accomplished by using an iodine saturator by passing some water through a bed of elemental iodine crystals. Detention in the iodine bed is maintained long enough to reach saturation. This iodine solution is then injected or pumped into the main water stream. Any desired dose can be attained

3.0
and maintained by this method provided certain limitations of the method are realised. The solubility of iodine is significantly dependent on temperature (Figure 1). Fortunately, in the normal range of water temperatures of about  $5^{\circ}$ C -  $20^{\circ}$ C the solubility curve is fairly flat so that the strength of the iodine solution will be in the range of 200-300 mg/l. A typical iodine saturator is shown in Figure 3. An alternative arrangement using a positive displacement metering pump is shown in Figure 4. This latter arrangement, while more complicated, is similar to a chlorinating facility but with automatic production of an iodine feed solution from iodine crystals. With a feed solution strength of 300 mg/l, iodine solution must be proportioned in the range of 1/600 to 1/300 to produce residuals in the range of 0.5 - 1.0 mg/l. At water temperatures below approximately 7.2°C (45°F) a contact time of at least 30 minutes is required for residuals of 0.5 - 1.0 mg/l and at water temperatures above  $7.2^{\circ}\text{C}$  at least 15 minutes is required. A storage tank of sufficient volume to achieve this retention time at the maximum flow rate must be fitted. If large storage reservoirs are used, providing retention times in excess of 6 hours, the free iodine residual will tend to disappear so that if a free iodine residual is to be maintained at the point of use, excessive retention times should be avoided. The use of flow control devices would appear to be highly desirable in a practical installation in order to limit maximum flow and hence retention time.

Indine up to a level of 1.5 mg/l is said to impart no taste or odour to the treated water.

## 3.2 Determination of Iodine Residuals

Iodine residuals may be determined by a number of methods -(a) DPD colorimetric, (b) orthotolidine (c) starch iodide,(d) Leuco crystal violet, (e) amperometric. The DPD method is probably the best colorimetric method. The orthotolidine test (5) requires modification for proper results. The Leuco-crystal violet method used by Black (6) appears to form the basis for both a field monitoring kit and a more accurate spectrophotometric lab test by the industry.

## 3.3 Biological criteria for evaluation

At the time, temperature and concentrations recommended for iodination in the commercial literature there should be no problem in completely inactivating the coliform group under most practical situations total coliforms in the raw water do not exceed where 1,000/100 ml. Figure 2 shows the time versus concentration relationship for  $I_2$  (and HIO) at 18°C. It will be noted from the graph at 0.5 mg/l and a 15 min. contact time at 18°C that there is a considerable safety margin for inactivation of E. coli. It should be noted, however, that depending on pH and therefore whether hypoiodous acid is present in significant concentration, there will only be marginal virucidal effects. No cysticidal (against E. histolytica) effects should be expected for the normal 0.5 mg-1.0 mg/l and 15-30 min. contact time. The limitations are those of concentration and time. Higher iodine concentrations could be used to give cysticidal and virucidal effects in 15 minutes but a de-iodination step using carbon would be necessary similar to that used in superchlorination/dechlorination practice. Filtration through at least a 5 µm filter would also ensure removal of cysts.

The disinfection efficacy of a particular installation designed to give at least 15-30 min retention time at a dose of 0.5-1 mg/l can be checked by the routine water sample examination procedures for coliforms available through the Provincial Health Laboratories.

#### 3.4 Iodine releasing resin type units

A number of small pour-through devices for water purification based on quaternary ammonium anion exchange resins combined with triiodide, are available from Water Pollution Control Systems, Texas. A larger home water treatment system complete with charcoal filtration, disinfecting resin bed, and pressure tank is also available. According to published work carried out at Kansas State University (7), contact with the resin beads is necessary for disinfection. No contact time after filtration is said to be required and iodine residuals in the filtrate are virtually nonexistent. The small units using the patented chemical resin triiodide, manufactured by Water Pollution Control Systems, Texas, have EPA registration for bactericidal effectiveness. These are the only small portable filter type units which we are aware of which have EPA registered bactericidal claims when used alone to treat water. (Other EPA registered products with bactericidal claims require pretreatment using hypochlorite for disinfection). It is understood that the triiodide resin system has been selected by NASA for treatment of drinking water aboard space shuttle flights.

# 3.5 Physiological effects of the long term ingestion of iodine

The work of Black et al (3) (4) between 1963 and 1965 has already been mentioned. Their studies indicated no harmful physiological effects to those consuming the water. Zoeteman (8), in a technical paper published by the World Health Organization in 1972, has critically examined the suitability of iodine and iodine compounds as disinfectants for small water supplies. He stated that "under poorly controlled circumstances ..... the low solubility of iodine, its good germicidal capability and its relative chemical inertness make it a suitable water disinfectant." However, certain reservations were expressed about concentrations of iodine required for "polluted waters with a high initial iodine demand, where physiologically toxic levels of iodine will be present." For this reason he felt that iodine disinfection should be limited to emergency use although it was admitted that the "risks of toxic effects, that have been found due to prolonged exposure ..... are very infrequent and transitory and are very minor compared with the risks of fatal enteric disease."

## 3.6 Manufacturers/Suppliers

Iodinamics Corporation P.O. Box 26428 El Paso, Texas 79426 U.S.A.

Can Aqua Corporation Limited 85 The East Mall Suite 110 Toronto, Ontario N8V 1A1

Water Pollution Control Inc. 6350 LBJ Freeway Dallas, Texas U.S.A. Trade Name/Model

"Iodinator"

"Iodion" Models:

Available as 1 lb, 3 lb, 5 lb, 15 lb, 25 lb, 50 lb, 100 lb and 200 lb systems. Corresponding to gallonage treated at 0.5 mg/l from 240,000 (l lb unit) to 48,226,000 gallons (200 lb unit).

- "Mini"II Pour-Thru. Effective maximum disinfecting capacity, 3,800 litres.
- "Puri-Jug". Effective maximum disinfecting capacity, 3,800 litres.
- "Maxi" Water Purifier ~38,000 litres disinfecting capacity

Home Water Treatment System  $\sim$ 7.6 to 11.4 1 per minute and a total disinfecting capacity of  $\sim$ 95,000 litres.

#### IODINE REFERENCES

- Chang, Shih L. and Morris, J.C. "Elemental Iodine as a Disinfectant for Drinking Water." Ind. Eng. Chem. 45, 1009, 1953.
- Morris, J.C. et al. "Disinfection of Drinking Water under Field Conditions." Ind. Eng. Chem. 45, 1013, 1953.
- Black, A.P., Thomas, W.C. et al. "Iodine for Disinfection of Water." J. AWWA, 60, 69, 1968.
- Thomas, W.C. Jr., Black, A.P. et al. "Iodine Disinfection of Water." Arch. Environ. Health, <u>19</u>, 124, 1969.
- Johanneson, J.K. "Determination of Microgram Quantities of free iodine using orthotolidine reagent." Anal. Chem. <u>28</u>, 1475, 1956.
- Black, A.P. and Whittle, G.P. "New colorimetric methods for halogen residuals." Water & Sewage Works, 114, 437, 1967.
- 7. Fena, L.R. and Lambert, J.L. "A Broad spectrum water disinfectant that releases germicide on demand" Proc. 2nd World Congress on Water Resources, New Delhi, India, December 1975.
- 8. Zoeteman, B.C.J. "The suitability of iodine and iodine compounds for small water supplies." Technical Paper No. 2, World Health Organization, International Reference Centre for Community Water Supply. July 1972, The Hague, The Netherlands.

3.7



Fig. 1. Solubility of iodine in water (concentration as a function of temperature).



Fig. 2. Time versus concentration relationship in the destruction of cysts, virus and bacteria by I and HIO at  $18^{\circ}$ C.



Fig. 3 Iodine saturator

OZONE

,

- 26 -

As a disinfectant for water, ozone has been used for municipal size plants for over 60 years, mainly in Europe. Studies (1)(2)(3)(4) have shown that ozone is a highly effective disinfectant for water which has bactericidal, virucidal and cysticidal properties. A comprehensive review of the use of ozone in water treatment by O'Donovan was published in 1965 (5).

## 4.1 Generation of Ozone and Biocidal Properties

Ozone is generally produced by three techniques, (a) silent arc (corona) electrical discharge, (b) electrolysis of perchloric acid and (c) ultraviolet lamps with output at 184 nm. Methods (a) and (b) give relatively high concentrations of ozone and method (c) considerably less. The electrical discharge method is the normal method used commercially for the generation of ozone. Basically this method consists of impressing an AC voltage of between 4 KV and 30 KV between two electrodes (plate or tube type) separated by a small air gap and dielectric. Air (or oxygen) is passed between the electrodes and ozone is formed in the corona. A typical commercial ozone system will consist of an air blower, air filter, air refrigerator and/or air dryer (desiccant), ozonator (either water or air-cooled), ozone injector or diffuser, and contact chamber. Commercial ozone generators operating with dry air or oxygen (dried to -50°C) will produce about 1% w/v of  $0_3$  with air and about 2% w/v with oxygen. At an AC frequency of 50/60 cycles about 17 watts of electrical energy per gram of ozone produced from dry air is required.

There are a number of variables involved which make it difficult to predict accurately the dosage of ozone required to disinfect a given water. The following biocidal activity of ozone has been found. The lethal concentration for <u>E. coli</u> suspensions at 1°C was found by Ingols and Fetner (6) to be that quantity of ozone required to produce a free ozone residual in the water which in this

4.0

case was about 0.4 to 0.5 mg/l. Newton and Jones (3) found that ozone dosages of 4.7 to 5.1 mg/l gave complete destruction of 3000 to 4000 cysts of E. histolytica at the end of 5 minutes contact time. It was also estimated that 96-99% of the cysts were destroyed in the first minute. With residuals lower than 1.8 mg/l viable cysts were recovered. As far as viruses are concerned a 1 mg/1 ozone residual at the end of a 4 minute contact time appears to ensure 99% inactivation of polioviruses (7). In general it appears that with water with low ozone demand the usual dosage of 1.5 to 2 mg/l of  $0_3$  is reasonable as far as bactericidal effects are concerned, provided a trace of  $0_3$ residual is achieved. For cysticidal and virucidal effects higher doses and residuals are required but the relationships of inactivation versus dosage and residual are, at present, poorly defined. This is mainly owing to the difficulty of applying ozone because of its poor solubility and the problem of measuring low residuals at short contact The effect of pH on disinfecting ability is relatively times. unimportant with ozone. Dissolved or particulate organics and inorganics in the water with an ozone demand, i.e. capable of being oxidized by  $0_3$ , greatly affect the required  $0_3$  dosage.

In addition to its biocidal properties ozone can also be used for the elimination of iron and manganese and for improvement in taste and odour. Ozone rapidly oxidizes manganese and iron into their insoluble salts. There are limits, particularly in manganese concentration, beyond which color is adversely affected because of the production of manganese dioxide. Filtration after ozone treatment is required to remove the oxidized mineral particles. According to Whitsun (8) the optimum dose for taste and odour control seems to correspond with the critical dose for disinfection.

In general, ozone is capable of disinfecting, eliminating certain tastes and odours, and removing color. However, it is not possible on the basis of evidence to date to predict results or dosages required. Actual tests are required to determine the effectiveness of ozone on a particular water.

## 4.2 Determination of ozone residuals

The most common procedures are (1) to use neutral KI solution and add the ozonated water (or bubble the ozonated gas), acidify to pH 2 and titrate the iodine liberated with thiosulphate using starch as an indicator, and (2) the DPD method in which ozone and diethyl p-phenylene diamine are reacted in the presence of KI. The intensity of the color developed is proportional to the ozone concentration. This method can be used in the field with reagents in tablet form and the results read against a color comparator.

#### 4.3 Ozone Water Purifiers for the Home

Only one manufacturer (Alron) appears to be actively promoting the use of ozone equipment for home water purification. At least two other companies in the past have offered similar equipment - Ozonator Corporation, Batavia, New York and the Compagnie des Eaux et de l'Ozone (CEO). The latter company is active in the ozonation of municipal water supplies and may still be able to offer small ozone generators for household use.

The Alron equipment is available in three model sizes according to technical data provided. A portable model (WP-4) is claimed to be suitable for treatment of water with bad odour, color, iron, manganese, sulfur (hydrogen sulfide), gases, volatile contaminants, chlorine, oxidizable or filterable organic impurities, and bacteria and viruses. The water source may be river, lake, spring, well or city water but it is not recommended for water with more than 5 mg/1 iron and sulphur. The unit comes complete with ozonator, a 5 gallon plastic purifying tank and a 5 gallon storage tank. The unit is said to be capable of batch treating 15 litres of water in the normal recommended purifying time of 15 minutes. A catalyst to decompose excess ozone in the exhaust gas is fitted. Filtration through a washable and removable fiberglass filter is accomplished during transfer (manual) of the treated water to the storage container. The two large automatic water

purifiers (WP-30 and WP-360) are said to have the same capabilities with the following exceptions. For these models it is recommended that surface water (river, lake etc) or turbid water be prefiltered. The units are not recommended for water with a total of more than 15 mg/l iron, sulfur, organic matter and other oxidizable contaminants. If these conditions are encountered the manufacturers recommend in the case of the WP-360 model that the flow rate be lowered or an ozone booster unit installed. Post filtration is required with both units, using either a cartridge or automatic backwash filter. The WP-30 unit normally operates on a minimum 5 minute ozonation cycle which is automatically activated by withdrawal of water from the tap. The size of the contact tank is not specified but the maximum water flow which can be purified is 115 litres/hr. In the case of the WP-360 model the contact tank size is stated to be 20 gallons (76 litres) which would give a theoretical retention time of slightly over 3 minutes at the maximum flow rate of 1364 litres per hour (22.7 1/min).

## 4.4 Criteria for evaluation

While ozone treatment can, when properly applied, handle several water problems such as taste, odour, color, bacteria at the same time, there is a paucity of information on dose and/or residual ozone/time relationship for efficacy. The ozone production rate, efficiency of transfer of ozone in the contact tank, etc. are not given in the technical literature supplied with current models of home water purifiers so that it is difficult to judge efficacy. If the philosophy is one of over or super ozonating (i.e. similar to superchlorination/dechlorination) the water to achieve the óbjectives, then some means should be provided for ozone residual tests to be carried out by the householder to ensure that an ozone residual (even if it is only a transient residual) is being obtained at maximum water flow or at the end of a batch treatment cycle. Fig. 1 shows a typical decay curve for residual ozone in water. The ability to test for an ozone residual in the water(before final filtration if a carbon filter is used) would give some assurance that disinfection is being achieved at the time. At present the only way a householder can verify adequacy of disinfection is to send samples of the treated water to the Provincial Health Laboratories for coliform counts. The standard collection bottle provided, which contains thiosulphate, is satisfactory for neutralizing ozone treated water. The greatest problem, in the opinion of the writer, with small ozone equipment using silent arc methods of generation, is drying of the incoming air. If this feature is absent or inadequate, then ozone output can vary drastically (see Figure 2) depending on the moisture content of the air. In addition, not only is ozone production diminished but oxides of nitrogen are produced at higher water vapor concentrations. These oxides of nitrogen accelerate the decomposition of ozone, accelerate corrosion of metals, and give rise to nitrates in the water. The small Alron WP-4 model does not appear to employ air drying equipment and no information on air drying is given in the technical literature for any of the models. There are recommendations for operating Models WP-30 and WP-360 in the range of  $5^{\circ}$ C to  $43^{\circ}$ C and a maximum humidity of 70%.

It is recommended that suppliers of home water purifying ozone equipment furnish minimum data outlined in "Proposed Ozone Standard Specifications" by the IOI Standards Committee (see copy attached). Information on items OlD, OlE and, in particular, OlF on production ratings would be highly desirable.

Claims to remove toxic organics with ozone such as insecticides would require efficacy data (see section on suggested test protocol for toxic organics removal). Claims to remove iron, manganese and hydrogen sulfide may be accepted on the basis of residual ozone being present in the water. Alron of Canada Division of John A. McManman Ltd. P.O. Box 220 Shanley Road Cardinal, Ontario

Distributor: Ronco Company P.O. Box 351 Cambridge Preston, Ontario N3H 4T3

1

## Models

Alron Portable Water Purifier Model WP-4. 15 1 in 15 minutes in a batch process.

Alron "Mini" Automatic Water Purifier Model WP-30, 115 1/hr.

Alron Automatic Water Purifier Model WP-360

# OZONE REFERENCES 1. Kessel, J.F. et al "Comparison of chlorine and ozone as virucidal agents of poliomyelitis virus." Proc. Soc. Exp. Biol. & Med. <u>53</u>, 71, 1943. 2. Smith, W.W. & Bodkin, R.E. "Influence of hydrogen ion concentration on the bactericidal action of ozone and chlorine." J. Bact. <u>47</u>, 445, 1944. 3. Newton, W.L. & Jones, M.F. "The effect of ozone in water on cysts of E. histolytica." Amer. J. Trop. Med.

Dickerman, J.M. et al. "Action of ozone on water borne bacteria."
 J. New England Water Works Assoc. 68, 11, 1954.

29, 669, 1965.

- 5. O'Donovan, D.C. "Treatment with ozone." J. AWWA 57, 1167, 1965
- 6. Ingols, R.S. & Fetner, R.H. "Some studies of ozone for use in water treatment." Proc. Soc. Water Treatment and Examination, 6, 8, 1957.
- 7. Katzenelsen, E.H. et al. "Ozone inactivation of water-borne viruses." Proc. 4th Scientific Conf. of the Israel Ecological Soc., Tel Aviv, 1973.
- Whitsun, M.T.B. "The treatment of water by ozone."
   J. Inst. Civil Engineers, <u>21</u>, 83, 1943.

- 32 -

4.6



100 % of rated ozone production 50 +10 -0 -10 -20 -30 -40 -50 -60Dew point of air-°F

Figure 2

"An International Organization for the Transfer of Technology in Ozone and related Oxygen Species Sciences"

# PROPOSED OZONE STANDARD SPECIFICATIONS

ΒY

# IOI STANDARDS COMMITTEE

# 01 OZONE GENERATOR SPECIFICATIONS

The following description gives the minimum data that shall be furnished by any Ozonator Manufacturer when specifying or quoting Ozone Generators.

# 01A WATER COOLED OZONE GENERATORS

1-Ozone Generator Type \_\_\_\_\_rated to produce \_\_\_\_\_\_ Ibs/Hr of ozone at \_\_\_\_\_% concentration by weight (or volume) from (air or O2) dried to -60°F (-50°C), supplied to the ozone generator at \_\_\_\_\_scf/hr, at \_\_\_\_\_psig and a temperature of not over \_\_\_\_\_°F. The Ozone Generator to be furnished with \_\_\_\_\_Volts, \_\_\_\_phase \_\_\_\_Hz power by the customer and its full load requirements will not exceed \_\_\_\_\_KW and \_\_\_\_\_KVA. The Ozone Generator must be furnished \_\_\_\_\_gph of cooling water at \_\_\_\_\_°F and the temperature rise in the water will not exceed \_\_\_\_\_°F.

# 01B AIR COOLED OZONE GENERATORS

1-Ozone Generator Type \_\_\_\_\_ rated to produce \_\_\_\_\_ lbs/Hr of ozone at \_\_\_\_\_% concentration by weight (or volume) from (air or O2) dried to -60°F (-50°C), supplied to the Ozone Generator at \_\_\_\_\_ scf/hr,at \_\_\_\_\_ psig and a temperture of not over \_\_\_\_\_ °F. The Ozone Generator to be furnished with \_\_\_\_\_ Volts, \_\_\_\_\_ phase \_\_\_\_\_ Hz power by the customer and its full load requirements will not exceed \_\_\_\_\_ KW and \_\_\_\_\_ KVA. The Ozone Generator must be furnished with \_\_\_\_\_\_ scfm of cooling air at \_\_\_\_\_ °F and the temperature rise in the air will not exceed \_\_\_\_\_ °F.

#### THE INTERNATIONAL OZONE INSTITUTE 24 CENTRAL AVENUE WATERBURY, CONNECTICUT 08702

Proposed Ozone Standard Specifications -- contd.

# 01C Measurement Systems

The English or Metric System of measurement may be used, at the option of the manufacturer or customer.

# 01D Production Ratings

For standardization, the production of all Ozone Generators should be given on the basis of 1% concentration by weight in air, or 1.7% concentration by weight in oxygen. When necessary to specify an Ozone Generator at other concentrations, data should be furnished to show its capabilities at the recommended concentration.

- 01E For standardization, all Ozone Generators should be rated on the basis of the cooling medium (water or air) being furnished at 70°F or 21°C. If there is to be a variation in the supply temperature of the cooling medium throughout the year, or the Ozone Generator must be quoted at another temperature, then curves, or other data, should be furnished to show production changes in the temperature of the supplied cooling medium.
- 01F Production ratings are based on the Ozone Generator being furnished with normal filtered pure air or oxygen. In many cases the Ozone Generator must operate with air or oxygen containing known impurities, or additives. In these cases, the manufacturer should supply the normal production rating of the Ozone Generator and that with the impurities, or additives.

# 01G AUXILIARY EQUIPMENT

Ozonator Manufacturers often supply Auxiliary Equipment for various purposes, such as drying the feed air, purification of the recycled oxygen, cooling the ozone generator, or other purposes. Technically, this equipment does not come under the scope of the International Ozone Institute. As it is often necessary to the proper operation of an Ozone Generator, it is recommended that the manufacturer supply complete details to the client, and specifically including the KWH and other requirements, such as cooling water or air.

# ULTRAVIOLET WATER PURIFIERS

.

### ULTRAVIOLET WATER PURIFIERS

## Introduction

5.0

The effectiveness of ultraviolet light as an agent for the inactivation of microorganisms has been recognized for many years. Studies have shown that the individual wavelengths of monochromatic ultraviolet radiation have varying germicidal efficiency, the peak effect being observed at a wavelength of 265 nm.

Luckiesh and Holliday (1) showed that the mathematical relationship between the survival rates of <u>E. coli</u> and exposure to ultraviolet energy was as follows:

$$\frac{N}{N_{o}} = e^{\frac{-Et}{Q}} \qquad \text{or} \qquad N = N_{o}e^{\frac{-Et}{Q}}$$

Were

N is the number surviving N<sub>o</sub> is the number before treatment E is the intensity of ultraviolet t is the exposure time Q is the exposure (Et) termed a unit lethal exposure

For the medium water and <u>E. coli</u> organisms this exposure (Q) is found to be 40 microwatt-minutes per square centimetre.

Thus the degree of kill is mainly dependent upon the intensity x time, of irradiation, although departures from expected death rates are common in practical situations owing to factors such as clumping of microorganisms, shielding by particulate matter and degree of agitation or turbulence. A number of UV purifying units have been designed on the basis of the above equation with safety factors of two or more.

#### 5.1 Sources of UV and their characteristics

#### Emission of UV

Low pressure mercury lamps with a quartz bulk are the most common sources used to produce UV radiation falling within the germicidal spectrum for UV water purifiers. These lamps are similar in construction and operation to ordinary fluorescent lamps except that UV lamps have no phosphor and have a quartz bulb. Over 85% of the UV radiation emitted from such lamps is at 253.7 nm, close to the optimum germicidal wavelength.

### UV/Ozone production

In addition to emitting 253.7 nm germicidal radiation, low pressure mercury lamps emit a certain amount of radiation at other wavelengths in the UV region. One wavelength of practical interest is that emitted at 184.9 nm. This radiation is very effective in forming ozone from oxygen in the atmosphere and depending on the "glass" used, lamps are obtainable with the same transmission for 253.7 nm but having a transmission of around 10%, 1.5% and 0.1% at 184.9 nm so that the quantity of ozone produced varies from fairly large to a negligible amount. At least two manufacturers of UV water purifiers claim that hydrogen peroxide (or some OH radical) is produced in small quantities in water by such lamps with high output in the 184.9 nm region. This "peroxide" residual is said to enhance the germicidal action of the 253.7 nm radiation.

Other factors affecting lamp output are voltage variations, frequency of the supply and age (i.e. number of hours of burning) of the lamp.

#### Temperature effects

The optimum operating temperature for low pressure mercury lamps is 40°C. Operation of such lamps at lower ambient temperatures markedly reduces output. For example, at  $\sim$ 5°C lamp output at 253.7 nm is about 20% of that produced at  $\sim$ 40°C. For this reason most UV lamps used in water disinfection have a quartz sheath and air gap interposed between the lamp bulb and the water flow to protect against adverse cooling.

#### Voltage

A drop in line voltage from 110v to 100v has been stated by Courtelyou (2) et al to reduce intensity by 22%.

## Frequency of supply

The writer has observed that frequency of the line supply can affect UV output. UV purifier units using a lamp and ballast designed for 115v 60 cycle AC supplies showed a reduction of about 30% in output when operated on a 115v 50 cycle supply. While this factor is not important on the North American continent it could be important in the performance of models exported or supplied to other countries using 50 cycle AC supplies or used in emergency field conditions on power derived from motor generator sets. When operated on AC, an arc goes out at the end of each half cycle and must start again on the next half cycle. This can only occur if some ions remain in the space in the interval between half cycles. If the time interval becomes too long the gas has time to deionize, and the arc fails to be maintained.

## Age of lamp

The UV output of a new lamp drops by about 20% in the first 100 hours of operation. Thereafter, only a slow change is observed and at the typical 7500 life rating,output is still about 70% of that when new.

#### 5.2 Measurement of dosage - physical detectors and biological detectors

According to R.W. Yip and D.E. Konasewich (3) two functions of the physical sensing system should be distinguished (a) measurement of the relative decrease in the intensity of the UV light incident on the water (I<sub>0</sub>) due to lamp aging and deposits formed on the quartz sleeve, (b) monitoring the % transmission (%T =  $\frac{I}{I}$  x 100, where I<sub>0</sub> is the intensity of the incident light and I, the intensity of the transmitted light) at 253.7 nm of the water in the UV chamber. The dosage (D) in the case of (a) is linearly dependent on the incident light (I<sub>0</sub>) but in (b) is not necessarily linearly dependent on %T due to non-uniform flow pattern in the reactor. As a result the efficacy of a particular UV purifier unit must be determined empirically by absolute dosimetry using bacterial inactivation rates under dynamic conditions at a particular flow rate or rates. This empirical method does, however, take into account flow pattern, UV intensity and absorption characteristics of the water.

Most UV water purifiers of the domestic type, if fitted with a UV detector, measure only I, the light transmitted through the fluid, so that there is a non-linear relationship between dosage and % absorption. Nevertheless, by the use of a UV meter with a narrow spectral response at 253.7 nm and calibrated against an NBS standard germicidal lamp, it is possible to correlate UV transmission of the water, flow rate and the numbers and types of microorganisms to be inactivated, to the UV output of the particular equipment.

#### Inactivation dosages

In arriving at a suitable UV exposure (time x intensity) the resistance of the microorganisms to UV inactivation must be taken into account.

#### Bacteria

Nagy (4) reported in 1955 that <u>E. coli</u> has a greater resistance than other water borne pathogenic bacteria. Huff et al (5) in 1965 also were of the opinion that <u>E. coli</u>, as a representative of the coliform group, and because it has comparatively greater resistance than other enteric pathogens, should be an adequate bacteriological test organism for evaluating the effectiveness of treatment of drinking water by UV irradiation. These authors found in an evaluation of a commercially manufactured UV disinfecting system that, provided the radiation dose did not fall below 11,000 µwatt sec/cm<sup>2</sup>, the system gave satisfactory results. At this dosage a safety factor of 1.6 was estimated for <u>E.coli</u> as determined by breakdown in treatment efficiency at two flow rates. An excellent review of UV disinfection and evaluation of a commercially manufactured UV unit has also been given by Oda (6) in 1969.

## Viruses

Nagy (4) and Huff <u>et al</u> (5) also conducted virus inactivation studies and demonstrated that provided the total dose did not fall below 11,000  $\mu$ watt sec/cm<sup>2</sup> and virus levels were below 1,000 PFU (plaque forming units) per milliliter, the enteric viruses (Polioviruses I, II and III,ECHO 7 and Coxsackie A9) were inactivated. Vajdic (7) in 1969 also found that where initial virus (bacteriophage) levels were in excess of  $10^4$ /ml, during UV irradiation in a commercial unit,breakthrough occurred. From this and other work (8) the consensus of opinion is that UV treatment appears to be capable of producing a virus-free effluent when viruses are present in the raw water at levels found in polluted surface waters.

## Protozoa

The cysticidal properties of UV are largely unknown although it has been established that UV is lethal to the cysts of the intestinal pathogen, <u>Endamoeba histolytica</u> (9) Unfortunately, this work did not establish the exposure (µwatt sec/cm<sup>2</sup>) required for inactivation. Although <u>E. histolytica</u> is not a protozoan of much concern at the present time in Canada there are other protozoans which should be given consideration. These are <u>Giardia lamblia</u> and <u>Naegleria gruberi</u>. An outbreak of giardiasis was reported in Rome, New York (10) in 1975 and traced to a marginally disinfected (chlorination), <u>unfiltered</u> municipal water supply coming from a predominantly rural area. <u>Naegleria gruberi</u>, a free living amoeba, is of concern in bathing waters and has been found to cause meningo-encephalitis in man.

It is therefore suggested, in the absence of definitive cysticidal properties for UV, that filtration ahead of ultraviolet disinfection be employed not only to remove turbidity and particulates which could adversely affect the UV disinfection, but to remove cysts as well. In order to do this it is suggested that a filter capable of removing particles down to about 5µm be employed, ahead of the UV unit.

## 5.3 Interferences

There appears to be no consistent quantitative relationship between units of color as determined by standard analytical methods and decreased UV transmission. Similarly, turbidity units as determined by light scattering techniques do not necessarily correlate with a reduction in UV intensity so that in general, units of color and turbidity are not adequate measures of the decrease that may occur in UV transmission. Humic substances and iron in the water are two materials which do interfere with UV transmission. If dissolved iron is present in the ferrous form it is likely to plate out in the less soluble ferric form on the quartz tube or sheath of the apparatus. It is, therefore, highly desirable that before installation of a UV water purifier, the UV transmission of water source be known. Most manufacturers recommend filtration before UV treatment and if iron is present, a manganese green sand filter to remove suspended solids and dissolved iron.

## 5.4 Criteria for the Acceptability of an Ultraviolet Disinfecting Unit

In 1966 a policy statement on the use of ultraviolet processes for disinfection of water was issued by the Public Health Service of the United States' Department of Health, Education and Welfare. This bulletin also contained criteria for the acceptability of an ultraviolet disinfecting unit. A copy of this bulletin is attached.

In 1975 the Department of Health, Education and Welfare further interpreted the standard calling for an ultraviolet dosage of 16,000 µwatts/cm<sup>2</sup>, redefining the dosage term by adding the following: "Acceptable ultraviolet units must have a flow rate that does not exceed 2/10 of a U.S. gallon per minute per effective (arc length) inch of ultraviolet lamp. The ultraviolet lamp must emit germicidal energy (253.7 nm) at an intensity of 4.85 ultraviolet watts per square foot

- 41 -

at a distance of 2 inches or an equivalent ratio of lamp intensity to flow rate. For example, a lamp with output of 9.7 ultraviolet watts per square foot will permit a flow rate of 4/10 of a U.S. gallon per minute per inch. The purification chamber shall be so designed as to guarantee a minimum of 15 seconds retention time at the maximum flow rate of the system."

At present there are three basic size UV lamps which conform to the output requirement of 4.85 UV watts/sq. ft at 2 inches. These have effective arc lengths of 30", 58" and 60". Thus, a 30" lamp can treat up to 6 USgpm (22.8 1); a 58" lamp 11.6 USgpm (44 1) and a 60" lamp 12 USgpm (45.6 1).

## 5.5 Types of commercially available UV units

UV water purifying units obtainable from the manufacturers listed may be classified as follows:

- Units which use a quartz jacket to protect against temperature effects.
- 2) Units which have no jacket where the lamp is in direct contact with the water to be treated.
- 2) Units which utilize lamps with significant 184.9 nm output and which produce an oxidizing residual  $(H_2O_2)$  in water.

Units in the first category typically consist of a metal or plastic tube approximately 100 mm in diameter. Mounted centrally in this tube is the UV source enclosed in a tube or sheath of quartz of diameter approx. 50 mm. The annular space between the sheath and the outer container acts as a disinfection chamber through which the water is passed. Turbulence promoting devices such as a helical baffle, are sometimes used. The tube sizing and equipment dimensions are selected on the basis of bacterial load and the UV transmission characteristics of the raw water. Most units are designed to provide in excess of 30,000  $\mu$ watt sec/cm<sup>2</sup> at the design flow rate with a new lamp and usually not less than about 20,000  $\mu$ watt sec/cm<sup>2</sup> after 7500 hrs of burning. These units therefore generally can be shown to satisfy criteria 1, 2 and 3 of the USPHS criteria for acceptability, although they may not satisfy the 15 sec residence time requirement of the revised 1975 criteria. Units in the second category (no jacket) would not meet Criterion 3a. Low pressure mercury lamps (Hg pressures of  $10^{-3}$  to  $10^{-2}$  mm Hg) require a fairly high striking voltage to start but full UV output is available almost immediately at ambient room temperatures. The need for a time delay mechanism as specified in the USPHS criteria to permit a two minute tube warm up is, in the writer's opinion, not mandatory if low pressure mercury lamps operating at ambient room temperatures (i.e. jacketed tubes) are used and the unit is normally left on. It is suggested that unjacketed UV devices be thoroughly checked for starting ability and UV output against time at temperatures of 5-10°C since low temperatures could drastically affect lamp operation.

Automatic flow control valves to restrict flow to the maximum permitted for the particular unit are frequently offered as optional extras. Unless it can be shown by the manufacturer that the maximum design flow for the particular unit cannot be exceeded because of inlet and outlet orifice restrictions at a working pressure of 40-80 psi, it is strongly recommended that flow control devices be installed. The exposure to UV (time x intensity) is directly related to flow rate. All UV units should have flow restrictions to meet Criterion No.6 of the USPHS.

UV purifiers in the lower price range usually rely on visual checks to ensure the unit is "on" by providing a plastic capped sight port for observation of the visible blue light output of the lamp.

Accurately calibrated ultraviolet intensity meters are rarely fitted but are sometimes available as an accessory. The main reason is one of cost (at least \$200). Ultradynamics Corporation is one manufacturer known to offer a model calibrated within 3% of an NBS standard lamp at 253.7 nm. Fail-safe type, rather than calibrated, meters or monitors are more commonly offered as accessories along with a shut off valve (solenoid). Depending on the construction of the sensor and filters used, these devices may give relative UV readings on a meter scale with bands showing "good" and "replace." More often, however, the sensors respond to visible

blue light as well as UV and do little more than sense that the UV lamp is on. When coupled to a solenoid shut off valve even the poorest of these devices will, when operative, activate a solenoid or warning device if the UV lamp fails. Sensors which respond to visible light will not, however, activate an alarm or solenoid if UV transmission is cut down by UV absorbing substances in the water, e.g. iron or humic substances, turbidity etc. Unfortunately, solid state devices used in the sensor and electronics can fail in the "open" position so that true fail-safe operation in the event of failure of the monitor is not readily achieved. At least one manufacturer (Trojan) has tried to avoid this problem by offering a fail-safe device which senses current to the UV lamp. No details on this device are available at present and it is not known whether anything more than a "go/no go" operation type is being achieved. UV output is related to lamp current but the ratio of UV output to electrical input is in the region of 1:7 to 1:15 depending on the particular lamp.

Criteria 8 and 9 of the USPHS are therefore usually only partially met, if at all, by installing an optional monitor and solenoid valve.

Automatic audible alarms again are available as optional extras. However, if a fail-safe (solenoid operated) device is fitted, the failure to obtain a flow of water alerts the user to the problem.

The materials of construction of the units (stainless steel or plastic - commonly ABS) checked appear to meet Criterion No. 10 on lack of toxic effects from the materials of construction. (PVC pipe is not suitable for UV service unless special additives to improve resistance to UV are incorporated in the formulation).

A few manufacturers offer models fitted with manual or automatic wipers for cleaning the quartz sleeve (Atlantic Ultraviolet and Ultradynamics), others rely on pretreatment and filtration ahead of the unit to delay the requirement for cleaning until the lamp must be changed (e.g. Ultra Safe models and Trojan models). The Ellner (Erie Manufacturing) models have a port in the housing which apparently is to permit periodic chemical cleaning of the unit while in place. Details of the recommended cleaning procedure are not available from the company's literature but it probably consists of a mild acid wash using acetic acid.

In the writer's opinion only a "systems" approach can be taken to water purification. In the case of UV purifiers pretreatments include (a) removal of iron if above about 0.3 mg/l (manganese greensand or equivalent), (b) activated charcoal for removal of UV absorbing organics, filtration to remove suspended particulates. One or more of the (c) above pretreatments may be necessary depending on the nature and variability of the raw water source. Most UV manufacturers will test raw waters and recommend appropriate pretreatment if required. Filtration should always be considered in conjunction with UV to remove possible particulate matter and to remove protozoa and their cysts. Cysts of E. histolytica are 8-12 µm diameter and the small flagellated protozoan Giardia lamblia 12 µm. If cysts are considered to be a hazard filtration down to 5 µm should be considered. Even this might not give complete protection since, although rare, a "small race" of cysts of E. histolytica 4  $\mu m$  in diameter have been identified. Most cartridge type filters specified or supplied by UV manufacturers are in the range of 10-15 µm since the life of filters with smaller micron size retention becomes rather short.

#### 5.6 Biological criteria for acceptability

Although UV units may be designed to meet the physical criteria outlined in the USPHS document, the final proof of efficacy of the device is whether it will produce a disinfected water under the worst operating conditions likely to be encountered at the flow rate claimed. As already stated, the consensus of opinion is that the coliform group and <u>E. coli</u> in particular is a suitable test organism since the resistance of these organisms to UV is greater than other pathogenic enteric bacteria. (For the present it is assumed that cysts would be removed by prefiltration and that viral standards for water have not been set although UV is probably a more effective virucidal agent than most).

- 45 -

A coliform challenge of between 1000 and 5000 coliforms (or E. coli) per 100 ml immediately ahead of the UV purifier fitted with an aged (not <100 hours and preferably 7500 hours) lamp or lamps and operated at the design flow rate, is suggested. The rationale for suggesting this is that a typical UV water purifier installation is unlikely to employ more than single filtration and UV disinfection. Therefore, a total coliform level of between 1000 and 5000/100 ml immediately ahead of the UV unit (i.e. after any filtration device) may be judged a suitable challenge. It is recommended that effluent sample volumes of at least 100 ml be subjected to the membrane filter test or alternatively the MPN test. Techniques to maximize recovery of damaged coliforms in the MF method such as peptone water rinse supplemented with glutamate are recommended. Neutralization of samples with thiosulphate is required where manufacturers claim that their lamps produce  $H_2O_2$  residuals in water. The challenge test should be repeated at twice the design flow rate (if possible) and also at half the design flow rate in order to assess the safety factor and the effect of the design of the unit on flow patterns within the unit. Criteria for acceptance or rejection may then be based on the results obtained using the limits suggested for total coliforms in drinking water on page 8 of "Canadian Drinking Water Standards and Objectives 1968."

Most manufacturers of UV water purifiers (Ultradynamics, Aqua Pur, Trojan, Atlantic Ultraviolet) have published efficacy data based on similar challenges. Final proof of efficacy can be obtained from installed units in the field since the consumer can have the water supply examined, before and after UV treatment, by the routine sample bottle method established for examining water supplies by most provincial health authorities in Canada.

## 5.7 Recommendations

A survey of installed UV water purifiers is recommended in view of recent adverse bacteriological findings on UV purifiers aboard vessels reported to the"Drinking Water Disinfection ad hoc Advisory Committee" (Atlanta,Dec. 15-16,1976) of the U.S. Department of Health, Education and Welfare, and the growing popularity of this method for treatment of private water supplies obtained from wells, springs and lakes in Canada.

- 46 -

The following major manufacturers and/or suppliers have been

	identified:	•
	Manufacturer/Principal Supplier(s)	Trade names of equipment & models available
1.	Aqua Pur Inc. 110 Bessemer Rd. London, Ontario N6E 1R2	Ultra Safe C-400 ~11.5 1/min CVS-400 ~11.5 1/min C-300 ~30 1/min CVS-300 ~30 1/min Larger models to approx. 150 1/min
2.	Atlantic Ultraviolet Corp. 24-10 40th Avenue Long Island City,N.Y. 11101 U.S.A. Ralph E. Benner Ltd. 620 Supertest Downsview, Ontario	Sanitron Ultraviolet Water Purifiers Model A75 ~5 1/min "A75B ~5 1/min "A250 ~16 1/min "A600 ~38 1/min "A2400 ~150 1/min Larger Models up to approx. 1,260 1/min. B model operates on either AC or 12 DC.
3.	Ultraviolet Purification Systems Inc 109 Montgomery Avenue Scarsdale, N.Y. 10583 Made in Canada by:	. Ellner EP6 to EP120 with flow rates of ∿23 to 455 1/min
4.	Erie Manufacturing Co.(Canada)Ltd. P.O. Box 880 Stouffville, Ont. LOH 1LO and Erie Manufacturing Co.(Canada)Ltd. 8070 Chamilly Street St. Leonard, Que. H1R 2S4	Ellner TS405 * 18 1/min EP8 \u03b3 1/min EP8M \u03b3 0 1/min EP24 \u03b3 92 1/min EP48 \u03b3 1/min EP50 \u03b3 1/min EP120 \u03b3 455 1/min * Appears identical to Trojan TS405 model
5.	Multus (Katadyn) Guillot Inc. 1339 St. Hubert Montreal, Quebec	Multus Junior Type J80 1/min max.Multus U2/100200 1/min max.Larger models available to max. 3600 1/min.

Cont'd .....

- 47 -

	Manufacturer/Principal Supplier(s)	Trade names of equipment & models	available
6.	Trojan Environmental Products P.O. Box 2341 London, Ontario N6A 4G3 also available through Alron Ozone Water Purifier Environmental Products Ronco Co. (1976) P.O. Box 351 Cambridge, Ontario N3H 4T3	Trojan TS402-12 TS402-120 TS405 Model 402-12 operates from 12v DC. Corresponding Ronco numbers to above	l/min l/min l/min ve.
	Kinetico Inc. Newburg, Ohio 44015 U.S.A.	Sunlite K-402-12 7.6 K-402-120 " K-402-12MV " K405-120 19 K405-12 " K405-12MV " MV models have shut off valve.	1/min " 1/min "
7.1	Ultradynamics Inc. 80 West Street Englewood, N.J. 07631 U.S.A. No Canadian representative at present. Units are sold directly to Canadian customers.	Models       100       6         Models       250       16         500       32         Larger       models       to approx.	l/min l/min l/min l/min
8.	Aquafine Corporation 1869 Victory Place Burbank, California 91504	Aquafine SL10A ∿11.4 SL1 ∿38 Nine other models with capacities 38 1/min to ∿500	l/min l/min of l/min

#### Ultraviolet References

- 49 -

- Luckiesh, M. and Holliday, L.L. "Disinfecting water by means of germicidal lamps." Gen. Electric Rev. <u>47</u>, 45, 1944.
- Courtelyou, J.R. et al. "Some physical factors affecting the effectiveness of germicidal ultraviolet radiation. Appl. Microbiol. 2, 269, 1954
- 3. Yip, R.W. & Konasewich, D.E. "Ultraviolet sterilization of water - its potential and limitations." Water & Pollution Control, June 1972
- Nagy, R. "Water Sterilization by Ultra-violet Radiation." Research Report B1-R-6-1059-3023-1. Westinghouse 1955.
- 5. Huff, C.B, Smith, H.F., Boring, W.D. and Clarke, N.A. "Study of Ultraviolet Disinfection of Water and Factors in Treatment Efficiency." Public Health Reports, U.S. Dept. of Health, Education & Welfare, Public Health Service, Aug. 1965, Vol. 80, No. 8, pp 695-705.
- 6. Oda, A. Ontario Water Resources Commission. Research Report No. 2012,1969.
- 7. Vajdic, Ann H. "The Inactivation of Viruses in water supplies by ultraviolet irradiation." Ontario Water Resources Commission Research Report No. RP2015, June 1969.
- 8. Hill, W.F, Hamblet, F.E. and Benton, W.H. "Inactivation of Poliovirus I by the Kelly Percy ultraviolet seawater treatment unit." Appl. Microbiol. <u>17</u>, 1, 1969.
- 9. Stoll, Alice M, Ward, P.A. and Mathieson, D.R. "The Effect of Ultraviolet radiation on cysts of Endamoeba Histolytica."
- 10. Morbidity and Mortality. 24, 43, 366. Center for Disease Control, US Dept. of Health, Education and Welfare, Atlanta, Georgia (Week ending 25/10/75).

#### DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE PUBLIC HEALTH SERVICE

Division of Environmental Engineering and Food Protection

#### Policy Statement on Use of the Ultraviolet Process for Disinfection of Water

The use of the ultraviolet process as a means of disinfecting water to meet the bacteriological requirements of the Public Health Service Drinking Water Standards is acceptable provided the equipment used meets the criteria described herein.

In the design of a water treatment system, care must be exercised to insure that all other requirements of the Drinking Water Standards relating to Source and Protection, Chemical and Physical Characteristics, and Radioactivity are met. (In the case of an individual water supply, the system should meet the criteria contained in the "Manual of Individual Water Supply Systems", Public Health Service Publication No. 24.) The ultraviolet process for disinfecting water will not change the chemical and physical characteristics of the water. Additional treatment, if otherwise dictated, will still be required, including possible need for residual disinfectant in the distribution system.

Color, turbidity, and organic impurities interfere with the transmission of ultraviolet energy and may decrease the disinfection efficiency below levels required to insure destruction of pathogenic organisms. It may be necessary to pretreat some supplies to remove excessive turbidity and color. In general, units of color and turbidity are not adequate measures of the decrease that may occur in ultraviolet energy transmission. The organic nature of materials present in waters can give rise to significant transmission difficulties. As a result, an ultraviolet intensity meter is required to measure the energy levels to which the water is subjected.

Ultraviolet treatment does not provide residual tactericidal action. Therefore, the need for periodic flushing and disinfection of the water distribution system must be recognized. Some supplies may require routine chemical disinfection, including the maintenance of a residual bactericidal agent throughout the distribution system.

## Criteria for the Acceptability of an Ultraviolet Disinfecting Unit

1. Ultraviolet radiation at a level of 2,537 Angstrom units must be applied at a minimum dosage of 16,000 microwatt-seconds per square centimeter at all points throughout the water disinfection chamber.

2. Maximum water depth in the chamber, measured from the tube surface to the chamber wall, shall not exceed three-inches.
- 3. The ultraviolet tubes shall be:
  - a. jacketed so that a proper operating tube temperature of about 105° F. is maintained, and
  - b. the jacket shall be of quartz or high silica glass with similar optical characteristics.

4. A flow or time delay mechanism shall be provided to permit a two minute tube warm-up period before water flows from the unit.

5. The unit shall be designed to permit frequent mechanical cleaning of the water contact surface of the jacket without disassembly of the unit.

6. An automatic flow control valve, accurate within the expected pressure range, shall be installed to restrict flow to the maximum design flow of the treatment unit.

7. An accurately calibrated ultraviolet intensity meter, properly filtered to restrict its sensitivity to the disinfection spectrum, shall be installed in the wall of the disinfection chamber at the point of greatest water depth from the tube or tubes.

8. A flow diversion value or automatic shut-off value shall be installed which will permit flow into the potable water system only when at least the minimum ultraviolet dosage is applied. When power is not being supplied to the unit, the value should be in a closed (fail safe) position which prevents the flow of water into the potable water system.

9. An automatic, audible alarm shall be installed to warn of malfunction or impending shutdown if considered necessary by the Control or Regulatory agency.

10. The materials of construction shall not impart toxic materials into the water either as a result of the presence of toxic constituents in materials of construction or as a result of physical or chemical changes resulting from exposure to ultraviolet energy.

11. The unit shall be designed to protect the operator against electrical shock or excessive radiation.

As with any potable water treatment process, due consideration must be given to the reliability, economics, and competent operation of the disinfection process and related equipment, including:

1. Installation of the unit in a protected enclosure not subject to extremes of temperature which could cause malfunction.

2. Provision of a spare UV tube and other necessary equipment to effect prompt repair by qualified personnel properly instructed in the operation and maintenance of the equipment.

3. Frequent inspection of the unit and keeping a record of all operations, including maintenance problems.

SILVER - BACTERICIDAL

#### SILVER

#### Introduction

The use of silver as a germicide and its "oligodynamic" action has been known for about 100 years. The term "oligodynamic" was used to distinguish between the effect of silver nitrate solutions in concentrations of 10 mg/l or more and silver ions in very small amount - 50 to  $100 \mu g/l$ . The term means "effect or power in small amounts." Although many theories have been put forward on the mechanism of oligodynamic action of silver the literature on the effectiveness of silver in water disinfection is confusing and contradictory. Reviews by Woodward (1) and Romans (2) indicate the lack of agreement in the results by various investigators.

The bactericidal properties of silver have been studied by Wuhrman and Zobrist (3) using the usual indicator organism, <u>E. coli</u>. These workers showed that the inactivation (a 99.9% kill of <u>E. coli</u>) follows a first order reaction and that temperature, pH, concentration of silver and time of contact affected the results. A rise of  $10^{\circ}$ C decreased the kill time by a factor of 1.6, and increasing the pH by one unit also decreased the kill time by a factor of about 1.6. The significant findings from these studies, as far as water disinfection is concerned, is that concentrations of  $50 \mu g/1$  (the maximum permitted in drinking water) or less required quite long contact times to effect kill, e.g. at 25°C, pH 7.5, 32 µg/1 required 90 minutes, at 5°C and a pH of 7.5  $34 \mu g/1$  required 270 minutes.

# 6.1 Interferences

The antimicrobial action of silver is also subject to the following interferences:

#### Chlorides

Wuhrman and Zobrist found that the presence of 10 mg/1 chlorides increased the contact time required for a 99.9% kill about 25% and 100 mg/1 chlorides increased the kill time by about 70% for water treated with  $\sim$ 60 µg/1 silver.

#### Hardness

The same authors noted that for each 10 mg/l of hardness at 20°C and pH 7, the time required for a 99.9% kill increased about 3 minutes.

#### Phosphates

Phosphates interfere with the bactericidal action of silver, according to Wuhrmann et al (3) and Chambers & Proctor (4). Although not of significance in water disinfection, this factor is important in laboratory evaluation work since phosphate buffers are frequently used to prepare stock suspensions of organisms, in rinse water, etc.

#### Sulfides

Sulfides are said to interfere and it has been suggested that the maximum allowable sulfide concentration in water to be treated by silver be limited to 1 mg/1.

#### Dissolved Oxygen

Lack of DO in the water, according to Wuhrman et al, can drastically affect the bactericidal action of silver. A 50% increase in contact time was required for a water with no DO compared to one containing a DO of 8.7 mg/l to effect a 99.9% kill.

# 6.2 Water Purifiers using Silver

There are numerous water treatment devices incorporating silver as an antimicrobial agent. These products may be divided into two groups:

(1) Those which can be used on a raw water and are either bactericidal (or completely remove bacteria by filtration) and

(2) Those devices which are intended to improve the organoleptic qualities of an already disinfected, usually potable quality municipal water. These devices employ silver as an antimicrobial agent to control the growth of organisms in the activated carbon filter. Also in this group there are portable hand held units which, in addition to their use for taste and odour improvement of potable water, are also recommended for use with water of unknown bacteriological quality after the water has been disinfected with hypochlorite (bleach) solution or Halazone tablets. In this application the units per se are not claimed to "disinfect" but are said to remove objectionable taste and odour of residual disinfectant.

# 6.3 Bactericidal silver units

Most units which now lay claim to disinfecting water with silver use a filtration step designed to filter out bacteria. A list of the devices with disinfection claims is given in the manufacturers and distributors list. In the case of the Sterasyl and Katadyn products a ceramic filter candle is used, and in the case of the Filopur/Ogden and Sysc-RO units a membrane is used for filtration.

### Sterasyl and Katadyn units (porous ceramic filters)

The Sterasyl purifiers consist of a cylindrical element or candle with a hollow centre. Water is filtered from outside the cylinder to the hollow core. The ceramic material is composed of a mixture of clays and diatomaceous earth of porous structure. Suspended particulates larger than 1 µm in size are retained on the outside surface of the cylinder and the element can be cleaned periodically by brushing under running water. The ceramic candle is also impregnated with silver, and bacteria retained in or on the filter are either killed or their growth inhibited by contact with silver ions. The silver also prevents bacteria from growing through the walls of the element. (Water filters using an unsilverised ceramic element require periodic sterilization by boiling). According to the manufacturer's tables the life of the filter (250 mm ceramic cartridge) is about 2 years when delivering 30 litres water per day with silver residual of 0.02 mg/l. At 30 litres per day, with a residual of 0.04 mg/1, life of the cartridge is said to be 1 year. The Super Sterasyl model contains activated carbon within the

- 54 -

hollow ceramic core and is designed to dechlorinate (if used on a chlorinated supply) and improve the taste and odour quality of the drinking water. Maximum flow rates with a single cartridge is about 1 gal/min at normal line pressures.

The Katadyn filter candle is similar to the Sterasyl filter with silver finely distributed through the ceramic tube. The core of the cylinder is, however, also filled with silver quartz. The function of this latter material, according to the manufacturer's literature, is to prevent penetration and growth of bacteria from the outlet side. A number of different models of the Katadyn filter are available, from a pocket filter fitted with a hand pump capable of providing about 1 gallon of filtered water in 5 minutes to multiple cartridge in line filter models giving about 20 gallons/min.

#### Filopur (Ogden) and Sysc-RO Units (membrane filtration)

The Filopur water purifiers appear to contain a double filter cartridge consisting of a fibrous filter and a membrane filter, the latter having a pore size of 0.45  $\mu$ m. Although not stated in the manufacturer's brochures, the "self sanitizing" feature of the filter results from the use of silver. Presumably a core of silver/activated carbon is used either between the fibrous filter at the membrane filter or ahead of both filters. Two Model series are available, the "A" series containing an FP-1 type cartridge and the "BT" series containing an FP-2 cartridge. Flow rates obtainable during the functional life of the cartridge ( $\sim$  450 litres) for the "A" series is about 1.2 l/min. For the BT series, the life of the cartridge is about 900 litres at a flow of  $\sim$ 3 l/min. @ 50 psi.

The System 1 Sysc-RO reverse osmosis unit consists of a silver carbon cartridge incorporating  $5 \ \mu m$  filtration and an RO cartridge, together with a small (2-1/2 US gallon) plastic storage tank with automatic shut-off valve. The unit is designed for use in a pressure water system and is suitable for applications where relatively small quantities of demineralized and purified water are required. The RO section of the unit is designed to operate at between 40 and 100 psi with  $\sim$ 10% water recovery and will produce up to 19 litres per day (5 gal). Recommendations are that the cartridges be changed at about yearly intervals although no guarantee on life of the filters is given. A larger system Sysc-ROHC is designed for cold water dispensers or hot beverage dispensing machines with an output of approx. 24 1/hr cold and 12.7 1/hr hot water.

# 6.4 <u>Criteria for evaluation of bactericidal silver or silver/carbon</u> <u>containing filter units</u>

Interim Standards for Water Purifiers were issued by the EPA in 1975. In Section IV of the EPA document the use of pesticidal filters (or water-purifiers) on impure raw waters for (a) rural areas for routine home use and (b) as an emergency source of supply for campers, hikers, tourists, etc. were considered and were expected to meet the following bacteriological challenge. The test protocol consisted of using sterile dechlorinated tap water seeded with E. coli (ATCC11229) at a level of 200,000 to 300,000 microorganisms/ml with bacteriological and silver determinations made at three specified intervals after holding periods (if any) prescribed by the manufacturer. Bacteriological assays were to be conducted on two, one hundred ml samples at each interval, usually the beginning, middle and end of estimated filter life. To the two samples and the control at each time interval 1 ml of sterile neutralizing solution containing 5% sodium thioglycollate and 7.3% sodium thiosulphate were to be added after any prescribed holding period. The standard MPN fermentation tube test with lactose broth and direct plating of dilutions of test and control waters was requested, the latter to be made on Difco Tryptone Glucose Extract Agar. Since pure cultures were used no differentiating medium was necessary. The protocol, however, did state that if a naturally contaminated raw water was tested appropriate differential media must be employed. The interim standard therefore appeared to imply that

tests with coliforms in raw water might be acceptable, as well as data from the artificial contamination with E. coli.

A second procedure issued by the EPA and published in the Federal Register <u>41</u>, No. 152, Aug. 5, 1976 is more specific and is directed toward bacteriostatic filters whose primary function is the removal of undesirable substances such as chemicals, odours, color and particulate matter from municipally treated or other treated potable water, i.e. an already disinfected water. This test protocol, although it applies to bacteriostatic filters for potable water use only, does incorporate a very useful challenge test. Scheduled in the test at the 50% and 95% filter life is a 24 hr retention (no flow) of water seeded in this case with <u>Pseudomonas fluorescens</u>, at a concentration of approximately 500/ml. This holding period within the filter, of water containing microorganisms, more closely simulates the non-use or stagnation period expected under conditions of home use. This is a useful concept.

The Water Quality Improvement Standards and Certification Council (WQISCC), in interim draft No. 4 of Proposed Standards for Water Treatment Devices, proposes not only daily stagnation periods but also an operating duty cycle of 10% on 90% off, with a 15 to 40 minute cycle. The cycle to be continued for not more than 16 hours per day, 7 days per week. Two longer shutdown (stagnation) periods at 30% and 90% of the rated life for 60 hours are suggested for bacteriostatic units.

The operating duty cycle of 10% on 90% off in a 15 to 40 minute cycle for 16 hrs/day is an excellent idea and, together with stagnation periods, should simulate household conditions. The operating times are sufficient to accomplish accelerated life tests in a 2-3 month test program for those silver devices capable of processing fairly large volumes of water. It is recommended that similar stagnation periods and duty cycles be used to test bactericidal units, as suggested on the following pages.

# 6.5 <u>Suggested test protocol for bactericidal filters</u>

For testing bactericidal filters it is suggested that an unchlorinated or dechlorinated tap water with the following approximate composition -

TDS	200-600 mg/l			
рН	6.0 to 8.0			
Non-purgeable	TOC Not less than 2.0 mg/1			
Turbidity	Less than 1 JTU			
Temperature	5° to 25°C			

be seeded with either a stock E. coli (ATCC11229) suspension to a level between 1,000 and 5,000 organisms/100 ml or preferably with a mixed microbial population (including coliforms) by seeding with raw sewage to approximately the same level for total coliforms. A manifold arrangement and reservoir for microbial seed similar to that shown in Fig. 1 may be used so that multiple units may be run at the same time. A minimum of 3 filters of the same type but from three different batches should be run. One of the filters should be an "aged" filter from a batch manufactured 3 months before to ensure that the bactericidal agent and its release characteristics do not change with age. Following initial start-up procedures and after adjusting pressures and flow rates to the manufacturer's suggested levels, influent and effluent samples for bacteriological and chemical (silver) analysis should be taken. (It is suggested that automatic flow regulating devices be used to control flow at the required levels). The samples for bacteriological analysis should be taken directly into flasks containing 1 ml of neutralizing solution containing 5% sodium thioglycollate and 7.3% sodium thiosulfate per 100 ml of sample. If available, 5 ml of modified Dey/Engley medium per 100 ml sample of neutralizing medium of the following composition should be used instead of neutralizer. The use of this neutralizing medium has been found, in our experience, to give slightly better recovery of organisms in the membrane filtration procedures.

Universal D/E Neutralizing Medium (5	)	(modified)
--------------------------------------	---	------------

Bacto Tryptone	5.0 g
Yeast Extract	2.5 g
Sodium Thioglycollate	1.0 g
Sodium Thiosulfate	6.0 g
Sodium Bisulfite	2.5 g
Tween 80 (Polysorbate 80)	5.0 ml
*Lecithin (Soybean)	7.0 g
Water	1000 ml
рН	7.6

 Lecithin is L-α lecithin derived from soybean (Sigma Biochemical).

NOTE: Lecithin is difficult to dissolve. Add 7 grams lecithin to 500 ml distilled water, heat slowly to boiling and then add remaining 500 ml of water. Leave at 60-70°C for one hour with stirring for complete mixing and suspension of lecithin.

Bacteriological assays on the filtered water, after neutralization of silver, should be conducted in duplicate on at least 100 ml aliquots by the membrane filter technique for coliforms, with Tryptone Glucose Extract Agar (TGEA) as medium if the pure culture <u>E. coli</u> challenge is used and Endo LES as differential medium where raw sewage has been used. Where raw sewage has been used as seed, standard plate counts should also be carried out on duplicate 100 ml (membrane filter technique), 10 ml and 1 ml (standard plate count) samples, using TGEA. Incubation temperature may be standardized at 37°C for all counts.

The cycle of operation 10% on, 90% off with a 15 to 40 min. cycle (e.g. 3 minutes on, 27 minutes off) may be continued for not longer than 16 hrs/day 7 days/week. Samples for influent and effluent bacteriological and chemical (silver) analysis should be taken, preferably three times a week during the life of the unit (or a minimum

of 20 samples if the capacity and life of the unit is small) at approximately equally spaced intervals throughout the estimated life of the filter. Samples after the overnight stagnation period should be included, as well as samples under dynamic flow conditions. In addition, at the beginning and 95% of filter life analysis for pH, alkalinity, chlorides, sulfates, TDS, Ca, Mg, Na, total hardness and TOC should be carried out on the influent and effluent. Two special tests on a low total dissolved solids water (TDS) and high TDS water should be carried out at approximately 10% of life and immediately after 100% of life of the filter. The purpose of the two special waters is to provide extreme water chemistries for different "worst case" conditions. The low TDS, low pH water provides a worst case condition for possible excessive metal dissolution, and the high TDS, high pH water provides a worst case condition for possible bacterial overgrowth. The two types of water are particularly suitable for water filters employing silver as antimicrobial agent. Other products may require modification of the "worst case" waters. The low TDS test water may be prepared by partial demineralization and subsequent blending with the general test water and, if necessary, the addition of acid  $(H_2SO_A)$ to lower the pH to between 5 and 6.3). The low TDS should have the following characteristics:

TDS	<100 mg/1					
рН	Less	than	6.0			
Non-purgeable	TOC	Not	less	than	2.0	mg/l
Turbidity	<1 JT	U				
Temperature	5° to	o 25°	С			

The high TDS water may be prepared by the addition of sodium carbonate,  $CaCl_2$  and  $MgSO_4$  in approximately the same ratio as the general tap water to produce the following characteristics:

TDS	Not less than 800 mg/l			
рН	Above 8.0			
TOC	Not less than 2.0 mg/1			
Turbidity	<1 JTU			
Temperature	5° to 25°C			

For the low TDS and the high TDS tests sufficient water should be prepared to run one full day (16 hr) cycle on each water for the units under test. The low TDS and high TDS waters should be inoculated with <u>E. coli</u> ATCC1129 or with raw sewage to a level of 5,000 coliforms per 100 ml. Influent and effluent samples for bacteriological analysis and silver and chemical analysis should be taken after approx. 4 hrs of the 10% on 90% off cycle has been in progress. A final sample for bacteriological and silver analysis on influent and effluent should be taken after an 8 hr stagnation period after the end of the ~16 hr cycle. The low TDS test may be immediately followed by the high TDS water before returning to the life test cycle.

# 6.6 Information obtainable from suggested test protocol

If the above tests are carried out they should yield the following data:

- (1) The approximate life of the filter unit limited by
  - (a) breakthrough of coliform bacteria.
  - (b) clogging of the filter in the case of the disposable non-cleanable cartridge types.
  - (c) exhaustion of the silver.
- (2) Establish operation under two different adverse conditions with low TDS and high TDS water
  - (a) early in the life of the filter and
  - (b) at the end of the manufacturer's rated life of the filter.

If coliforms are found in the effluent at levels of 2/200 ml or levels approaching this in two consecutive samples the filter life time shall be revised downwards to the time (or volume) of the last negative sampling. If coliform breakthrough occurs initially in any sample filter the cause should be investigated and if no mechanical reason is found this should constitute rejection of the filters as bactericidal filters. Silver levels under all conditions should be <0.05 mg/l in accordance with Canadian Drinking Water Standards and Objectives 1968. A mechanical filtration function to remove cysts (5 µm or better) should be a requirement for all units claiming to have a bactericidal function.

# 6.7 Discussion on Neutralization of Silver

There is controversy on the need to neutralize the action of silver before plating out on media. It has been argued by some that, provided the samples are plated almost immediately into TGEA, this is sufficient to stop further action of excess Ag<sup>+</sup> in solution. The same group also is of the opinion that deliberate neutralization with thioglycollate and thiosulphate does not simulate what happens in real life, since the silver adsorbed on, or absorbed in, the bacteria is also neutralized as well as excess Ag<sup>+</sup> ions in solution, i.e. overneutralization occurs. The adsorbed silver on bacteria does need time to kill bacteria but it is maintained, on the basis of preliminary test data, that gastric juices do not affect recovery of silver-inactivated microorganisms. In other words, in a real life situation it is felt that Ag<sup>+</sup> inactivated bacteria will not recover when such water is consumed immediately after treatment with a silver releasing device. While there is some merit in this argument it is difficult to conduct experiments and plate out or, in the case of the test protocol suggested in this report, filter samples immediately and place on tryptone glucose extract agar. Most testing and regulatory laboratories would prefer to see a neutralization step. It has been our experience that the membrane in the membrane filter technique will adsorb Ag<sup>+</sup> or silver fines and, unless a neutralization step is included, erroneously low counts are obtained. To the best of our knowledge no convincing evidence has yet been presented to show that plating on TGEA alone, without prior neutralization, is sufficient to prevent bacteriostasis. In order to show that plating on TGEA is an acceptable practice it is recommended that tests be conducted to see whether bacteriostasis occurs after plating into TGEA. This can be done by adding a suspension of

- 62 -

a known number of viable untreated bacteria along with the treated suspension, to TGEA. If no bacteriostasis occurs, quantitative recovery of the viable suspension should be obtained. A sufficient number of tests by the pour plate technique and the membrane filter method, with control and test samples, would have to be carried out to statistically validate the findings.

For meaningful bacteriological data to be obtained from <u>bactericidal</u> silver units installed in the field it is recommended that 1 ml per 100 ml sample of 5% thioglycollate and 7.3% sodium thiosulphate (or modified Dey/Engley medium) be used as preservative in water sample bottles used by Provincial Health Laboratories for colliform enumeration. Thiosulphate alone has been shown to be insufficient (4). Silver devices - Bactericidal or disinfection claims

Manufacturer/importer/distributor Models Sterasyl Model CCO (W/O activated Envirogard Products Ltd. P.O. Box 64 carbon  $\sim 4.5 \ 1/min.$ Richmond Hill, Ontario Super Sterasyl Model SST (with L4L 4X9 activated carbon) ~4.5 1/min. Super Sterasyl Model SST2 (with activated carbon)  $\sim$ 7.5 1/min. Aqualine Products Ltd. 1677 Aimco Boulevard As above Mississauga, Ontario L4W 1H7 Also sold through Canadian Tire Stores Katadyn Type PF, pocket filter ∿l 1/min Katadyn, Guillot Inc. 6339 St. Hubert, Suite 314 Katadyn Type KFT, piston pump Montreal, Quebec filter  $\sim 3 1/min$ . H2S 2M1 Katadyn Type TRK disp. filter, may be fitted with 3 filter cartridges  $\sim$ 1.5 l per cartridge in 2 hrs. Katadyn Type HFK in line model ~2.5 1/min @ 70 psi. Katadyn Type MF3 in line model ∿7.5 1/min @ 70 psi. Other models to 77 1/min @ 70 psi Filopur "A" Series Filopur - Ontario Models AT1 Basic, AT1 plan 1, AF1 and P.O. Box Station A Ottawa, Ontario AFP1 all contain an FP-1 type cartridge. K1N 8V5 Type AFP1 is for use with a hand pump. Ogden Filter Co. Inc. 4222 Santa Monica Blvd. Ogden Models as above. Los Angeles, California 90029 U.S.A. Sysc-RO unit (System 1, silver-carbon-Water Purification Systems Inc. reverse osmosis)  $\sim 19 \ 1/day$ . 6502 NW 16th Street Plantation, Florida 33313 Sysc-ROHC for hot-cold water, ~24 1/hr U.S.A. cold water 50°F and 012.7 1/hr hot water. Water Purification Systems of Canada As above (G. Baudrieul) Montreal, Quebec (unable to locate)

6.9 Silver References

 Woodward, R.L. "Review of the Bactericidal Effectiveness of Silver" J. AWWA 55, 881, 1963.

2. Romans, I.J. "Oligodynamic Metals" Chapter 24 and "Silver Compounds" Chapter 28 of"Disinfection, Sterilization and Preservation" by Lawrence, C.M. and Block, S.S. Lea & Febiger 1968.

- 3. Wuhrmann, K. and Zobrist, F. "Investigations of the Bactericidal Effect of Silver on Water" Sweizerishe Z. Hydrol. <u>20</u>, 218, 1958.
- 4. Chambers, C.W. and Proctor, C.M. "The Bacteriological and Chemical Behaviour of Silver in Low Concentrations" U.S.P.H.S. Tech. Report W60-4, 1960.
- 5. Engley, F.B. and Dey, B.P. "A Universal Neutralizing Medium for Anti-microbial Chemists" CSMA Proceedings 56th Meeting, 1970.



BACTERIOSTATIC FILTERS (SILVER/ACTIVATED CARBON UNITS)

# BACTERIOSTATIC FILTERS (SILVER/ACTIVATED CARBON UNITS)

A large number of activated carbon based units intended to improve the aesthetic quality of potable water by removing (1) undesirable tastes, odours and colours and/or (2) reducing or removing contaminants in water which are established or potential health hazards, have appeared on the market. Most of these units employ about 0.5 to 1% of silver on the activated carbon to control the growth of microorganisms. A major supplier of silverized carbon to the industry appears to be Ionics Inc. This material is said to contain metallic silver deposited on the carbon by a process akin to silvering of a mirror. Other proprietary formulae using silver oxide, silver chloride and metallic silver are also being used. The bacteriostatic type activated carbon filters include portable hand held units and models for attachment to a faucet or for in-line installation serving a cold water tap or taps used for drinking water or culinary purposes. Prior to 1976 numerous claims have been made for these "purifiers", including bactericidal claims. The bactericidal claims for silver/carbon filters now appear to have been withdrawn, or at least restricted, to defined conditions of use. For example, (a) the Puritron unit (Water Purification Technology Inc.) implies a bactericidal effect after a 24-hour holding period after filtration of water, although for raw water, pretreatment with Halazone tablets is suggested; (b) the Mini-Silverator plus Mini-Booster (American Water Purification Inc.) recommended treatment for raw water is to add 5 drops of Mini-Booster (5% NaOC1) for disinfection, followed by filtration through the Mini-Silverator unit.

# 7.1 Bacteriostatic or Bacterial Reduction Claims

Since the units are intended for use on potable water supplies, disinfection is not a criterion but rather the control and/or reduction of "chlorine-resistant" organisms present in a municipal water supply.

Unfortunately, we are faced with a dilemma in choosing a test organism or organisms and in establishing a test protocol to evaluate claims. The following conflicting problems arise:

- If a chlorinated municipal supply water is used as test water this water will contain a chlorine residual in some form. This is desirable in so far as the background microbial population in the test water will contain chlorine tolerant organisms and therefore be typical of the microflora likely to be encountered in practice.
- A chlorine residual in the test water is undesirable from the point of view of adding a laboratory culture of challenge microorganism(s) since residual chlorine in the water will almost certainly affect the viability of the challenge microorganism(s). Thus it would be difficult to assess the antibacterial claims for the unit from the action of chlorinated water.
- Various test microorganisms have been advocated but to the best of our knowledge none offers the challenge of a natural aquatic flora already present in water. These naturally occurring organisms can show little or no reduction in numbers when tested in Ag/carbon units which had shown excellent control of, for example, E. coli. Other organisms which have been suggested are Serratia marcescens ATCC #14756 or ATCC #13880, preferably the latter strain which is an isolate from natural (pond) water. Pseudomonas fluorescens ATCC #13525 (EPA selection) and Pseudomonas aeruginosa. Serratia marcescens has characteristics similar to E. coli (both are enterobacteriacae) but may show high sensitivity to silver and therefore be unsuitable as a simulant. Tests with Pseudomonas fluorescens in one laboratory indicated that this organism did not remain viable over a 24 hour holding period in tap water. It might be profitable to examine several common water organisms (from municipal supplies) to determine if their reactivity to silver is similar. Choice of a moderate to high silver resistant strain would be desirable but final selection would have to include ability to remain viable when maintained in chlorinated tap water for a period of time.

It has been our experience that apart from any species differences in resistance, it is not easy to obtain reproducible resistance in laboratory cultures (particularly Pseudomonas spp.) and extremely difficult to obtain in laboratory cultures the same high resistance to antibacterial agents shown by natural waterborne organisms.

Some form of chemostat for growing microorganisms under natural conditions might be feasible and provide a solution to the problem. For example, if an activated carbon filter was connected to a chlorinated municipal supply it would rapidly become colonized with mainly chlorine tolerant organisms. The effluent could then be used to seed chlorinated water to challenge bacteriostatic units under test. Whether sufficient inoculum of chlorine tolerant organisms can be obtained on a continuous basis by this method for test purposes is not known. In addition, one species of organism would have to be enumerated in the influent and effluent of units undergoing tests since it is unlikely that the total microflora produced will show equal resistance (or susceptibility) to silver. This could be carried out in the study already suggested on resistance of common water organisms in municipal supplies to silver.

#### 7.2 Proposed test protocol for bacteriostatic silver/carbon units

Basically a general test protocol similar to that outlined for bactericidal silver devices is proposed. Assuming that a suitable test organism for challenge purposes has been selected following the studies suggested in the previous section, it is proposed that units be conditioned prior to the start of the test in accordance with the manufacturer's instructions, using the general test water specified in the bactericidal test protocol. A manifold arrangement for running three or more test units simultaneously, similar to that shown in Fig. 1 for bactericidal unit testing, is suggested. To ensure that the test set-up is suitable for bacteriological testing, test water should be sampled from the manifold at the start and at the end of a 60 hour stagnation period. If standard plate counts show a decrease in bacterial population during stagnation inside the plumbing of the module, the entire test procedure will be invalidated because of the presence of inhibiting materials. It is, therefore, important to verify the plumbing system before beginning the tests.

# General test

Install 3 or more units, from different batches, which have been preconditioned according to manufacturer's instructions. One of the units should be an "aged" sample from a batch manufactured approximately 3 months previously. Establish the recommended flow rate through each unit using the general test water given in the bactericidal test protocol but with a total chlorine residual of not less than 0.1 mg/1. Flow control devices may be required if the flow rate is not automatically controlled by orifices in the device. Start an operating cycle of  $\sim 10\%$  on, 90% off with a 15 to 40 minute cycle. This cycle should be continued for not more than 16 hours per day, 7 days per week and should include two shutdown (stagnation) periods of 60 hours at approximately 30% and 90% of estimated unit life. In addition to any naturally-occurring organisms in the water supply, the test organism (as yet unspecified) should be added to the general test water to produce a standard plate count (TGEA - Standard Methods for the Examination of Water and Wastewater 14th Ed.) of 500 to 5,000 per ml. At approximately five equally spaced intervals during the life of the filter the challenge should be increased to at least 5,000 per ml.

### Sampling

At the start of each operating day, i.e. after the overnight stagnation period, a first-flow sample should be collected from the influent manifold equal in volume to the stagnant water in the plumbing between the sample port and the nearest branch servicing a test unit (at least 50 ml). Immediately thereafter, a sample of one unit volume consisting of the stagnant water in the unit should be taken. The

- 70 -

sterile sample bottles should contain enough sterile sodium thiosulphate to neutralize any chlorine residual in the water, although this is only likely to be required where samples of influent under dynamic flow conditions are being taken. Immediately after collection the sample should be split for chemical and bacteriological analysis and the bacteriological analysis carried out immediately into TGEA medium. (Preferably prior neutralization with thioglycollate and thiosulphate or Dey Engley medium at the time the sample is split should form part of the test, if agreement on this procedure can be reached). Samples for silver analysis may be preserved with nitric acid. Within the last two hours of operation before each of the 60 hour periods of stagnation, manifold and effluent samples (dynamic flow conditions) should be collected as above and Standard Plate Counts carried out.

A low TDS test and high TDS test should be scheduled near the beginning and end of the unit life test. At least 100 unit volumes of the low TDS and high TDS water will be required. After approximately 80 unit volumes of the special test waters have been passed through the unit a stagnation period of 8 hours should be given before samples are taken in a similar manner to that described above. In addition, the test water should be analyzed to see that it meets the chemical requirements for a low TDS or a high TDS water. The high TDS test may be carried out immediately following the low TDS test.

If the flow rate of the test units is not automatically controlled a high flow rate test should be incorporated. The high flow rate test should be carried out at the maximum flow rate which can be produced with a 65 psi influent pressure for 100 unit volumes with the standard cycle. The high flow rate test may be carried out at 30% and 90% of estimated unit life prior to the 60 hour stagnation test. Samples should be collected during flow of the first 10 unit volumes and again during the last 10 unit volumes of the 100 unit volumes test. Flow rate should be returned to normal before proceeding with initial samples for the 60 hour stagnation test.

To qualify as a bacteriostatic unit the geometric mean of all the Standard Plate Counts of the effluent samples from each test unit should be no greater than 120% of the geometric mean of the influent samples.

If bacterial reduction claims are made the geometric mean of all the Standard Plate Counts of the effluent samples from each test unit should be no more than 10% of the geometric mean of the influent samples.

The following table summarizes the schedule of the proposed test protocol and has been adapted from the proceedings of the latest technical committee meeting (June 1977) of WQISCC, and should appear in similar or slightly modified format in the fifth draft of the proposed test protocols from WQISCC.

				Analysis	
Time		Activity	General Chemical	Silver	Bacteriological
Start up	<ul> <li>up          <ul> <li>Condition units according to manufacturer's specifications</li> </ul> </li> </ul>		<u>onemi cur</u>		
	•	Begin continuous bacterial challen with chlorinated general test wate	ge r		
	•	Begin regular on/off flow cycle	R	Х	R
2nd day	٠	Low TDS, low pH test	Х	X	
	•	High TDS, high pH test	х	Х	Х
20% life	•	Increase bacterial challengs to 5,000+/ml			x
30% life	٠	60 hour stagnation		Х	х
	•	* Bacterial acceptability test		Х	Х
40% life	•	Increase bacterial challenge to 5,000+/ml			x
50% life	٠	Water analysis	х		
60% life	•	Increase bacterial challenge to 5,	000/ml		Х
80% life	•	Increase bacterial challenge to 5,	000/ml		Х
90% life	•	60 hour stagnation		Х	Х
	•	Bacterial acceptability test		Х	Х
	•	High flow rate test		Х	Х
95% life	•	Water analysis	Х		
100% life	•	Increase bacterial challenge to 5,000+/ml			x
120% life	۲	Low TDS, low pH test	x	Х	
	٠	High TDS, high pH test	х	Х	Х
Each Mond	ay,				
Tuesday, throughou	Wed t s	nesday chedule • First water analysis		Х	Х

R - Recommended.

 Comparison of Standard Plate Count of influent water in manifold after stagnation and under flowing conditions. SPC under stagnant conditions should not show >20% decrease in SPC for test to be valid. /

#### Manufacturer/Distributor

American Water Purification 1990 Olivera Road Concord,California 94520 U.S.A.

No Canadian agent at present

Teledyne Water Pik Limited 1730 East Prospect Street Fort Collins, Colorado 80521 U.S.A.

Teledyne Water Pik Limited)82 Carrie Drive)Rexdale, Ontario)M9W 5R1)Also sold through Shoppers Drug Mart)

Water Safe Products Inc. 8337 Nieman Road Lenexa, Kansas 66214 U.S.A.

Canada Water Safe Products 931 Yonge Street Toronto, Ontario

Westinghouse Canada Limited ) Box 510 ) Hamilton, Ontario ) L8N 3K2 \* U.S. company appears to have gone out of business.

Silverator <sup>®</sup> Water Treatment Systems

- Mini Silverator portable, rechargeable, treatment capacity ~3,800 litres.
- (2) UTS Silverator under sink unit, rechargeable, capacity ~19,000 litres.
- (3) Home Silverator I and Home Silverator II capacities of 2.85 x 10° litres and 5.7 x 10° litres respectively.

With Silverator <sup>(R)</sup> pretreatment system becomes a chlorination/dechlorination system. See Chlorine section.

- (4) Mini Silverator + Mini Booster <sup>(K)</sup> for raw water uses hypochlorite solution (Mini Booster) and at least 10 min contact time before dechlorinating through the Mini Silverator.
- (5) Super Straw <sup>®</sup> pocket purifier, treatment capacity ∿38 litres. May be used with Mini Booster (hypochlorite solution).
- (6) Mini-Silverator Water Washer appears to be identical to Mini Silverator portable in (1) above.

Trade Name/Model

Instapure (TM) water purifier, treatment capacity  $\sim 1400$  litres - for attachment direct to tap or sink sprayer.

### Instant Clean

- (1) Model BAC-1 Bacteriostatic.
- (2) Model IC100 (carbon model).
- (3) The Traveler Model, TR-300 portable.
- (4) Model CM1000, 2000 and 3000.

#### Manufacturer/Distributor Trade Name/Model Water Purification Technology Inc. Puriton Bacteriostatic Drinking Water 527 Madison Avenue Treatment Unit New York, N.Y. 10022 U.S.A. - possible distributor: Mr. E. Matczynski As above. P.O. Box 302, Station F Toronto, Ontario M4Y 2L7 Hartford West Associates Mark I and Mark II Porta Pure Suite 112 4250 Pacific Hwy. San Diego, California, U.S.A. - not represented in Canada yet. Better Living Labs Inc. H2OK Water Purifier 2873 Director's Cove Memphis, Tennessee 38131 U.S.A. - not represented in Canada at the present time. PCP(TM) Pollution Control Products Inc. Mark L 1040 Bayview Drive water unit. Naturalizer Fort Lauderdale, Florida 33304 U.S.A. Aqua Purification Systems Inc. Mariner Water Renaturalizer 1001 Northwest 62nd Street Mariner AP3 1.9 1/min Fort Lauderdale, Fla. 33009 Filtration capacity ~7,600 1 U.S.A. Mariner AP3 CT As above, countertop model Mariner AP6 3.8 1/min Filtration capacity 57,000 1 Mariner Pretreated Water Unit 3.8 1/min

Filtration capacity 15,000 1

- 75 -

DISTILLATION TYPE WATER PURIFIERS

#### DISTILLATION TYPE WATER PURIFIERS

A number of small stills for the distillation of tap water, stream, lake or spring water or even salt water, are now on the market. A great deal of promotional literature regarding hazards and effects of poor water supplies on health and the benefits of drinking "pure" distilled water is associated with the sale of these devices. Distillation is usually described in the sales brochures as "nature's own method of water purification" or similar phraseology. While the documentation on the problems and hazards, both potential and real with regard to public water supplies, is impressive, little information is provided on what these small stills will do and their limitations when used to "purify" water. By and large it is assumed that no matter how polluted the water is, most, if not all, impurities are left behind on distillation and that the condensate is essentially safe, pure and wholesome.

#### 8.1 Distillation Units

The units consist of a metal or pyrex glass boiler fitted with an immersion heater, an air cooled condenser tube or condensing dome and a collecting reservoir for the distillate. Most units are designed for counter top use and manual filling of the boiler. Automatic shut-off of the cycle is provided. Larger units may be directly hooked up to a water line.

# 8.2 Limitations and potential problems

When used to distill municipal tap water few problems are likely to be encountered. It should be recognized that volatile organics (e.g. phenolics) will be carried over into the condensate and, depending on the volume collected, may actually concentrate volatile organics. Efficacy data on claims made or implied for removal of organics such as chloroform, pesticides, herbicides etc. should be backed by test data.

- 76 -

In other respects, such as mineral removal and bacterial removal, there is no reason why a water approaching USP distilled water standards cannot be produced. The materials of construction of the devices appear to be free from toxic hazards. The distilled water receiving containers may, after a period of time, become contaminated with Pseudomonas sp. since routine washing and cleaning of the container may be neglected by the user because it is only used to contain water. Information received on tests conducted by a U.S. laboratory on installations in the field indicate that microbial contamination of the distilled water reservoirs occurs quite frequently. Cleaning and descaling of the elements and boiler is likely to be a chore. Hazards most likely to be encountered are from touching heated parts and in some cases, fire and shock hazards. It is understood that recall was recently requested (October 1976) of the line of Aqua Water distillers and timers manufactured by the Pure Water Society of Canada Inc. because these units were not CSA certified and posed potential fire and shock hazard to the user. It is not known at this time whether the product line has been modified and received CSA approval.

### 8.3 Test protocol for efficacy of removal of organics

The test protocol outlined in the section on organics removal evaluation detailed elsewhere in this report should be used as a guide to obtain test data on the efficacy of removal of organic material. The life testing and ageing aspect of the suggested test protocol would not apply to tests on distillation units.

# 8.4 The following manufacturers and distributors of small portable stills have been identified:

	Manufacturer and/or Distributor		Trade Name/Models	Capacity
1.	Pure Water Society Inc. 3725 Touzalin P.O. Box 83226 Lincoln, Nebraska 68501 U.S.A.	) ) ) )	Aqua Clean <sup>TM</sup> Midi Still <sup>R</sup> Aquastill <sup>R</sup>	<ul> <li>4-5 US gallons/24 hrs</li> <li>∿8 US gallons/24 hrs</li> <li>13-15 US gallons/24 hrs</li> <li>Fitted with 5 gal storage tank.</li> </ul>
	Pure Water Society of Canada Canadian Head Office 1346 Ouellette Avenue Windsor, Ontario N8Y 1J8		Aqua Fountain <sup>TM</sup>	13-95 US gallons/24 hrs Fitted with a water chiller.
	Purewater Products (formerly Abso Pure Water Labs) P.O. Box 6216, Station "J" Ottawa, Ontario K2A 1T3	) ) ) )		
2.	Newater International Inc. A Division of Springsoft International Inc. 122 East Lake Street Bloomingdale, Illinois 60108 U.S.A. (No Canadian Distributor yet)		Newater Portable TM Distiller	1/2 US gallon per cycle, estimated 6-8 hours.
3.	New Medical Techniques Inc. Stamford, Conn. U.S.A.	) )	Aquaspring	$\sim 1/2$ US gallon in 7 hrs.
	EMF Novelties Import P.O. Box 669 Cobourg, Ontario K4A 2C9		Medi-Tech Hi-Speed	d ∿1/2 gallon in 2 hrs.
.

·

REVERSE OSMOSIS, ULTRAFILTRATION UNITS

# REVERSE OSMOSIS, ULTRAFILTRATION UNITS

Domestic type reverse osmosis (RO) units are designed to produce a small quantity of demineralized water from waters high in minerals such as sulphates or chlorides. The RO unit itself typically consists of a spiral-wound semi-permeable cellulose acetate membrane cartridge which when operated on household water line pressures (40-100 psi) will reject 80-95% of incoming dissolved minerals. Frequently, prefiltration of the water through a fine micron filter  $(5-20\,\mu\text{m})$  is employed to extend the life of the RO cartridge. If the water contains high amounts of iron or hydrogen sulfide more extensive pretreatment is used. During operation under pressure, continuous outflow must be maintained. Approximately ten times as much water (brine) flows to the drain as is collected (permeate) in the storage tank with these small domestic units. If this flow is shut off the membrane would rapidly become clogged. Most RO units therefore operate with only about 10% water recovery which means that for typical units producing about 5 gallons permeate per day, 50 gallons of water goes to waste. There are minor variations to this since at least one manufacturer uses an intermittent flushing feature to achieve recovery rates of 20-50 per cent.

Ultrafiltration units, as the name implies, perform a filtering action. Very small particles in solution or solids are separated from larger ones by a sieving action. Ultrafiltration units in operation do not differ materially from units performing an RO function. Ultrafiltration, as a term, is applied generally to the separation of solutes above a molecular weight of several hundred. There really is not a sharp demarcation line between reverse osmosis and ultrafiltration, and there is in fact a fair degree of overlap. In this report RO and UF systems will therefore be considered together.

9.0

### 9.1 Factors affecting or limiting RO performance

Actual performance of RO units is affected by a number of variables, the chief ones being:

- Pressure Both flux rate and rejection of salts vary with pressure. At low pressures (50 psi) both flux (gal/sq.ft/day) and rejection efficiency are lower than those obtained at, say, 200 psi with cellulose acetate membranes.
- Temperature Flux increases with temperature in the range 2°C to a recommended maximum of 38°C. Rejection of solutes is essentially constant with temperature.
- pH Cellulose acetate type membranes tend to hydrolyze. The rate depends on temperature and pH. The optimum pH (for low hydrolysis rate) is pH 5.
- Feed velocity High solute concentrations exist at the membrane surface unless flow conditions are such that turbulent mixing occurs. These effects are more severe at high flux conditions but are less likely to be encountered with the low flux, low recovery domestic RO units.
- Feed water recovery Rejection in the system tends to be greatest at low percent recovery so that this factor tends to offset the lower rejection efficiencies of operation at low pressures.
- Solute species Most inorganic species are well rejected, with divalent ions being especially well rejected. Rejection of organic molecules depends on their molecular weight and polarity.
- Fouling of Deposits of colloidal material, oils or precipitated salts the surface
   (e.g. Ca salts) will cause a flux decline. A pretreatment
   (and/or cleaning procedure, although this is not usually done
   with domestic cartridge systems) step using a fine filter
   (5µm) is often employed to reduce fouling of the membrane.

There are other factors such as hydrolysis of the membrane but this is unlikely to occur rapidly with waters between pH 5-8 and temperatures of 25°C. The support characteristics can also influence performance as in compaction of the membrane, but these are relatively unimportant in low pressure RO systems. Solute concentrations also have an effect but when dealing with most drinking waters the feed is unlikely to exceed 2500 mg/l of total dissolved solids so that this factor is less important.

## 9.2 Claims for RO systems

Claims are mostly for removal of salts and while a high general inorganic dissolved solids concentration is not considered a health related problem, it can produce unpleasant tastes and can create mild intestinal problems to people unaccustomed to such water. Claims for removal or reduction of organic pollutants from water are also made but many of the systems sold either incorporate pre and/or post filtration through an activated carbon bed so that removal of organics is likely to be accomplished by both carbon adsorption and RO rejection. Similarly, claims to remove the taste of chlorine from chlorinated water probably result from the use of a carbon filter. Chlorine above about 1 mg/1 has a deleterious effect on cellulose acetate type membranes. When used to treat municipal tap water the only problems likely to be encountered are proliferation of microorganisms in the system after dechlorination, particularly on activated charcoal filters and in the reservoir used to collect permeate. One manufacturer appears to have recognized this problem - Water Purification Systems SYSC-RO unit uses a silver/carbon filter ahead of the RO module and recommends clean-out of the storage container on a once a month basis.

# 9.3 Test protocol for particulate, inorganic and organic removal claims

RO units pose a special problem in lifetime type testing with particulate, inorganic or organic challenges since about ten times as much water is wasted to the drain (brine) as there is permeate. Nevertheless, brief challenge type testing using the same protocols mentioned elsewhere could be used, and the permeate collected and analysed during the challenge period. While this type of test would cover only one or two

- 81 -

complete cycles required to fill the reservoir with RO permeate, some indication of the on-line rejection performance of the units could be obtained.

# 9.4 Tests for bacterial control

It is suggested that the complete RO system should be subjected to tests on a chlorinated municipal supply for the period of the lifetime of the replaceable component with greatest life (probably the RO cartridge) in the system to see whether there is a buildup in total bacteria concentration in the final tap water. If high numbers of total bacteria are found after a period of time, it is suggested that they be assessed for potential health hazards, including endotoxin production. The following manufacturers and distributors of small domestic type reverse osmosis/ultrafiltration units have been identified.

## Manufacturer/Supplier

Culligan of Canada Ltd. Sheridan Park Mississauga, Ontario L5K 1A5

Universal Water Systems 1425 W. West Chicago, Ill. 60185 (Division of Coca-Cola, not yet available in Canada)

Purewater Inc. (Subsidiary Xonics Inc) 11085 Sorrento Valley Court San Diego, California 92121 (Not yet available in Canada)

Water Purification Systems Inc. 6502 NW 16th Street Plantation, Florida 33313 Aqua Clear  $^{R}$  Model H-5.  $\sim$ 20 litres/24 hours using 5  $\mu$ m prefilter

Trade Name/Model

RO unit, 13 quart reservoir and carbon adsorption filter. Acro Pac  $^{\rm R}$   ${\sim}20$  1/24 hrs with pre and post RO filtration.

Guardian System III<sup>TM</sup> Larger RO system to provide water for all household taps.

Purewater  $^{\text{TM}}$  Model 710-11  $\sim$ 20 1/24 hrs, no pre or post RO filtration, uses a flushing procedure.

System I<sup>TM</sup> SYNC-RO ∿20 1/24 hrs Silver/carbon filter followed by RO.

# ACTIVATED CARBON

### ACTIVATED CARBON

- 84 -

### Introduction

The occurrence of organic materials in raw water and potable water supplies can be readily demonstrated by measurement of nonspecific parameters such as TOC or COD and more specifically by gas chromatography and mass spectrometry. Recently the National Research Council \* in the U.S.A. has completed an 18-month study of drinking water and health. The report reviews the data available on water contaminants and, where possible, proposes maximum safe levels for these contaminants. The report indicates that in the area of organic contaminants in particular there is a lack of information to define safe levels, especially of those contaminants which are suspected carcinogens. For 45 compounds judged potentially toxic but not carcinogenic, where data were available, concentrations were found to be below the level likely to cause a hazard. Therefore, direct toxic effects of organic contaminants, although possible, are likely to be remote. Potential health hazards of carcinogenicity exist but the most common problem with potable water, as far as the consumer is concerned, is taste and odour. The use of activated carbon is often suggested as a solution to this problem and also for the removal of coloured contaminants. Although a considerable amount of information is available on adsorption characteristics of organic compounds, most data refer to high concentrations of organics and are of doubtful value in relation to concentrations found in water. A recent paper by Tebbutt and Bahiah (1) deals with adsorption of low concentrations of organics normally found in treated wastewater effluents and raw waters. For example, they noted that when mixtures of compounds of different adsorption characteristics were examined the overall isotherm curve became characteristic of unfavourable adsorption. Thus the degree of removal which can be expected using activated carbon in a given situation is very much a function of the concentration and types of organic material present in the water.

\* This report has just become available - only a summary of the data has been seen by the writer so far.

## 10.1 Activated carbon filter units

There are numerous manufacturers of activated carbon filters and only a partial listing of this large group has been made. These filters are often made in the form of replaceable cartridges for use in the home. Usually only the supply to the drinking water tap is filtered. Activated carbon filters are frequently used after a disinfection stage to remove the taste and odour of chlorine (e.g. in superchlorination/dechlorination or residual chlorine from municipal supplies) or to remove other taste and odour-causing substances such as chlorophenols. Claims are also often made that particulates and organics are removed as well. In this respect the claims are similar to those made for bacteriostatic type carbon filters, the essential difference being that the plain activated carbon units do not contain silver as an antimicrobial agent.

Depending on the size of the carbon bed, the type and form of activated carbon employed, taste, odour and colour-causing substances and a number of other organic substances will be removed to some extent. The life of such filters may be quite long for chlorine removal but quite short for other materials before breakthrough occurs. The industry has, however, used the removal of <u>free</u> chlorine as a successful indirect indicator of taste and odour removal over many years for activated carbon units.

The chief drawback to the use of activated carbon units is that they rapidly become colonized with bacteria and act as growth beds. As a result large numbers of microorganisms appear in the effluent water, particularly in the initial draw off of water after a period of stagnation. Table I shows typical counts from a carbon bed used after a halogen disinfecting device to remove residual halogens. It is for this reason that a number of manufacturers of water treatment devices employing activated carbon have incorporated silver in order to try to prevent such growth within the carbon bed.

Time	SPC/ml			
First flush	7,800			
l minute	50			
3 minutes	20			

### Table I

Standard Plate Counts in effluent stream from a carbon filter used for removal of residual halogens

It is not known whether such microorganisms constitute a direct health hazard but it has been noted that endotoxins were measurable in water after passage through activated carbon beds (2). The presence of endotoxins in drinking water does not seem to constitute a health hazard in normal subjects, according to DiLuzio and Friedmann (3) since absorption is limited. Jorgensen et al (2) point out, however, that the reticuloendothelial function can be altered by lead or other agents in the drinking water and, therefore, could interact with endotoxins in water to produce an endotoxemia in persons consuming such water. As far as we are aware, no studies on endotoxin production by bacteria growing in small activated carbon filters or silver/carbon filters installed in households have been carried out. It is suggested that this should be studied to determine the extent of endotoxin production.

There are two other causes for concern over high bacterial counts in water after filtration through activated carbon. These are (a) the possible loss of coliform test sensitivity in waters with excessively high bacterial populations and (b) the increased risk of human exposure to organisms that may be considered secondary pathogenic invaders.

## 10.2 Evaluation of carbon filters

Carbon filters may be subjected to the same test schedule suggested for bacteriostatic silver/carbon filters. Challenge to evaluate taste and odour removal ability may be based on using a challenge of 1.5 mg/l of free chlorine. Reduction to 0.1 mg/l or less should be achieved during the life of the filter. Challenges for removal of organics may also be incorporated into a similar schedule outlined in bacteriostatic filter testing but using the test protocols given in the section on trace organic analysis.

# Activated Carbon Filters

10.3

Manufacturer/ Supplier	Model (or cartridge) Number	
AMF Cuno	AquaPure Cartridge #AP117 ~11.25 1/min	
Division of AMF Incorporated 52 Roval Road	" " AP217 ∿ 7.5 1/min	5 µm
Guelph, Ontario, Canada	" " AP227 ∿ 7.5 1/min	5 µm
NIH 6NI	" " AP317 ∿ 1.9 1/min	5 μm
Universal Water Systems Inc.	Cartridge AGT - 200 $\sim$ 22.8 l/min	5 µm.
Division of Coca Cola 1425 West Harthouse Lane	" AGT - 250 ∿11.5 1/min	5 µm
West Chicago, Ill. 60185	" $T - 2 \sim 7.6  1/min$	5 μm
Water Equipment Technologies Inc. P.O. Box 14642 North Pole Beach Florida 33408 U.S.A.	. Waterbetter Cartridge #C-1-5 ∿7.6 1/min	5 μm
Ametek	Plymouth Cartridge #Cl $\sim$ 7.6 l/min	5 µm
Plymouth Products Division 502 Indian Avenue Sheboygan, Wisconsin, U.S.A. 53081 (Meek Sales Ltd. Bramalea, Ont. L6S 2E4)	" " C2 ∿ <b>15.</b> 2 1/min	5 µm
Everpure, Inc. 2213 N. Sheridan Way Sheridan Park Mississauga, Ontario. L5K 1H5	Everclear AC Cartridge min 2 1/min 1	μm
Omni Corporation 900 East 162nd Street South Holland, Illinois 60473	Omni Cartridge #TO1	

10.4 References

- Tebbutt, T.H.Y. and Bahiah, S.J. "Studies on adsorption with activated carbon", Effluent and Water Treatment Journal, <u>17</u>, 123, 1977.
- Jorgensen, J.H., Lee, J.C. and Pahren, H.R. "Rapid Detection of Bacteria", Applied & Environmental Microbiology, <u>32</u>, 347, 1976.
- DiLuzio, N.R. and Friedmann, I.J. "Bacterial endotoxins in the environment" Nature, <u>244</u>, 49, 1973.

FILTRATION UNITS - MISCELLANEOUS

# FILTRATION UNITS - MISCELLANEOUS

### 11.1 Commandment Industrial Limited KS22

11.0

The Commandment Industrial Ltd KS22 water purification unit consists of a hollow stainless steel perforated cylinder packed with activated charcoal and overlaid by a layer of fine mesh glass fibre and a layer of diatomaceous earth impregnated glass fibre. The water first passes through the glass fiber/diatomaceous earth layer, which is claimed to remove particles down to 0.5 µm; through the perforated stainless steel core packed with activated charcoal, and out through an end outlet fitted with a stainless steel strainer. During use the outer glass fibre impregnated layer becomes coated with a microbiological slime layer which is said to enhance the action and life of the filter. "Water Treatment and Examination" by Mention is made in Thresh (1) that a colloidal film will form on a fine mesh of material and act as a filter sufficiently fine to prevent bacteria and cysts from passing through. The filtered water from such filters is usually treated with a disinfecting agent. The KS22 filter could, therefore, be used as a pre-filter for raw water prior to disinfection or as a filter unit on municipal water. In the latter application the filter is said to give substantial removal of a variety of organic pollutants and to improve taste and odour. The claims made and life of such filters for potable supplies may be checked by using a similar test protocol to that proposed for testing bacteriostatic silver carbon filters except that Ag analysis would be omitted. The production of bacterial endotoxin may be a problem and it is recommended that tests for endotoxin be included in any testing.

11.2 Ambersorb (TM) XE-342 and Ambersorb (TM) XE-352

Very recently the Rohm & Haas Company has made available on an experimental basis macroreticular quaternary ammonium amine exchange resins which function as microfilters. Their large pore size of approx. 7 µm allows microorganisms to enter the pore cavity and be electrostatically bound to the surface of the resin. To prevent the trapped bacteria from growing and multiplying, the XE-342 resin contains 1-2% silver as a bacteriostatic agent. Ambersorb XE-352 contains no silver and is designed for use in larger installations where backwash of accumulating bacteria can be carried out. Ambersorb filters are said to effectively remove approximately 90% of E. coli for each six inch bed depth used in the column. For example, an inoculum containing approximately 25,000 E. coli/100 ml will show <2,500 cells/100 ml after passage through a six inch column; <250 with a 12 inch column; <25 with an 18 inch colum and <1 with a 30 inch column. These calculations apply to a system with linear flow rates up to 26 gpm/ft<sup>2</sup>. Similar effectiveness is claimed for S. faecalis, Pseudomonas aeruginosa, and it appears that a wide spectrum of microorganisms can be removed, suggesting that such filters may have general utility. The capacity of the resins is very high. For example, at an influent concentration of 25,000,000 cells/100 ml and a bulk flow rate of 0.6 gpm  $(23 \text{ gpm/ft}^2)$ , with a 3 1 volume of adsorbent in a bed of 48 inches, the total water processed, with a final concentration of <1 coliforms/100 ml, was 1,800 gallons. The filters are said to show gradual leakage of bacteria when they approach exhaustion.

It is expected that water treatment devices for industry and domestic use will be marketed using these resins. The only major drawback to the XE-342 resin is possible excessive (i.e. >50  $\mu$ g/l leakage of silver to the water at chloride levels in the incoming water water of less than 20 mg/l. Claims and life tests of AMBERSORB filters may be evaluated using the protocol suggested for bacteriostatic type Ag/carbon filters. 11.3 Manufacturer/Supplier

Commandment Industrial Ltd. (Klein Engineering Ltd) 2852 Flannery Drive Ottawa, Ontario KlV 8W4

Rohm & Haas Company Independence Mall West Philadelphia, Pa. 19105 U.S.A. Trade Name/Model

KS-22 - Capacity ∿1100 1/hr and and life of 3 to 5 years

AMBERSORB  $\underbrace{TM}_{TM}$  XE-342 (with silver) AMBERSORB  $\underbrace{TM}_{XE-352}$  (no silver)

11.4 References

 Thresh, J.C. "Water Treatment and Examination" Ed. W.S. Holden, 1970.

ORGANICS REMOVAL

. 

.

### ORGANICS REMOVAL

This section deals with the suggested testing protocol of purification units for their organics removal capabilities.

The general overview and the suggested testing protocol result from the following:

<u>1</u>. Critical evaluation of available literature with special reference to the articles cited below:

- (a) Analysis of organic compounds in water to support health effect studies, WHO International Reference Centre for Community Water Supply a consultant's report by Dr. A.W. Garrison. Technical Paper #9, December 1976.
- (b) Federal Register Vol. 41, #152, August 1976.
  Interim requirements for registration of bacteriostatic water treatment units for home use.
- (c) Water Quality Improvement Standards and Certification Council. Interim Draft #4, January, 1977. Proposed interim voluntary industry standards for portable, household and commercial units for treating water for human consumption.
- (d) Reported performance data determined for various water purifiers (including analytical techniques) by U.S. Testing Laboratories on commercially available units, e.g. Teledyne Water Pik (Jan. 1977) and Water Safe Products Inc. (Oct. 1975).
- (e) Environmental Protection Agency statement of work re
  "Organics removal capabilities of commercially available home water treatment units" - November 1976.

2. Ontario Research Foundation testing protocols for removal of specific trace organic components when evaluating the performance of client prototype water purifier units.

12.0

#### 12.1 INTRODUCTION

Drinking water will probably always contain large numbers of organic compounds. The important task is to determine which compounds are present in concentrations significant enough to pose a hazard to human health.

The analysis of water samples for organic contaminants is complicated by the wide range of concentrations that are encountered. The detection level adopted must be selected carefully because it determines the number of compounds that can be identified. The level must be low enough to reveal all important compounds but not so low that it makes analysis unduly difficult. A detection limit of  $10^{-1} \mu g/1$ is usually selected for drinking water and for water from most lakes and streams.

Recent disclosures with respect to the formation of potentially carcinogenic organics (trihalomethanes) by the chlorination of drinking water have caused concern with respect to the quality of drinking water. Many new home water treatment units have appeared on the market and consequently there is a need to verify the claimed performance capabilities of such units.

Chemical removal units are usually classified by the specific contaminants removed rather than by the process or method of operation. They all commonly use processes such as absorption, adsorption, distillation, ion exchange or membranes.

When checking the performance of home water treatment units it is well to remember that standard tap water will be used that has been spiked with known compounds at predetermined concentrations. This is very important with respect to the choice of the analytical method to be used when analyzing the effluent from the units. The detection level limit can be selected to suit a particular method of analysis for the chemical(s) used as spike(s).

An outline test protocol for use in assessing the performance of home water purifier units for the removal of specific organics is given below. When testing units for organics removal it is preferable to be specific, e.g. chloroform rather than volatile halogenated organics (VHO); dieldrin rather than chlorinated pesticides. However, total organic carbon (TOC) is used as a parameter to measure polar compounds and non-purgeable organics present in tap water. Furthermore, it is desirable to provide multi-test set ups so that up to five (5) units can be under test at the same time. This can be a very important time saving feature.

#### 12.2 OUTLINE OF TEST PROTOCOL

- 1. The test procedure should simulate in-use conditions.
- 2. Tap water spiked with various standard chemicals is run through the test units at the recommended flow rates and at ambient water temperature using a predetermined cycle, e.g. 20 min off/2 min on. For long life units accelerated testing will be required. As a general rule a unit test should not be accelerated so much that the entire run requires less than five (5) real days [unless the unit fails in less than five (5) equivalent days or more quickly than expected]. It is desirable that an overnight holding period of 8 or more hours be provided between each test day.
- 3. Standard chemicals are to be spiked at 2 to 3 times the maximum contaminant level (MCL) or at other levels acceptable to the government body which will assess the results. Where no maximum contaminant level has been established or where maximum contaminant levels are high, a challenge of 2 to 3 times maximum levels found in untreated or community treated water may be used. The standard chemicals to be used for spiking will include some or all of the following:
  - (i) Trihalomethanes specifically chloroform.
  - (ii) Organochlorine pesticides (selected from Aldrin, DDE, dieldrin).
  - (iii) Chlorophenol specifically 2,4-dichlorophenol.
- 4. For a given unit it is suggested that analyses be performed at the start, 25%, 50%, 75% and 100% of lifetime. An estimate of probable

lifetime to be used for determining sampling events. In practise, samples should be collected every day, preserved and stored for possible future analysis. These subsequent analyses will be based on the 5 event analysis data mentioned above, and will be devised to include and more fully define the zone of failure.

### 12.3 ANALYSES

It is recommended that tap water used shall average not less than 2 mg/l non-purgeable total organic carbon (NPTOC) in order to be acceptable as providing adequate conditioning for the units.

The usual water analyses - conductivity, pH, TDS, total hardness, alkalinity - should be performed at each sampling interval for both influent and effluent water to the unit.

The major challenge for organic removal with test units should involve worst case testing of chloroform at 2 to 3 times the maximum allowable contaminant level. (Chloroform was found in 95% of the finished waters examined in the EPA National Organics Reconnaissance Survey undertaken in the USA to provide an estimate of the nationwide distribution of organics in drinking water).

Other organics, e.g. dieldrin, 2,4-dichlorophenol could be run at the same time as the chloroform by providing a "cocktail mix" of the specified organics in a challenge solution. The requirement to test a specific "cocktail mix" rather than an individual specific chemical will depend on availability of funds and also the claims of the manufacturer with respect to the unit under test. A "cocktail mix" would be the preferred method if removal of a spectrum of specified organics is being claimed. Studies on adsorption with activated carbon indicate that when mixtures of compounds of different adsorption characteristics are run, the adsorption isotherm data become less favorable.

The preferred method for the analysis of low levels of chloroform (and other trihalomethanes), i.e. <1  $\mu$ g/l, is that of Bellar and Lichtenberg(1,2). In this procedure the sample is purged with an inert gas that is passed, in series, through an adsorbent material that traps and concentrates the organic material. The organic is then removed from the trapping material by thermal desorption and transferred to a gas chromatographic column for analysis. Detection and quantitation is achieved using a Hall Electrolytic Conductivity detector operated in the specific halogen mode.

A sampling procedure is chosen that provides minimum loss of the volatile organic to the atmosphere while the sample is awaiting analysis. The containers should be vials (50 ml capacity) that can be sealed with Teflon-faced "Tuf-bond" discs. When sampling, the vial is filled, bubble free, to overflowing so that a convex meniscus is formed at the top. The excess water is displaced as the disc is carefully placed, Teflon side down, on the opening of the vial. An aluminum seal is then placed over the disc and crimped into place. A sample taken in this manner will be completely headspace free at the time of sampling. Collected samples should be refrigerated until analysed.

The level of organic challenge to the unit will, however, allow other more rapid analytical procedures to be used. Direct aqueous injection of the sample into the gas chromatograph is the simplest procedure available. The method as described by Nicholson and Meresz (3) for the detection and estimation of trihalomethanes by direct aqueous injection using electron capture detection, is a suitable procedure where the concentrations of trihalomethanes are expected to be at a level of 5  $\mu$ g/l or higher.

Also two solvent extraction methods outlined in recent publications (4, 5) on rapid and sensitive methods for determining volatile organohalides in water could be used. These papers describe procedures using solvent extraction (Methylcyclohexane and Pentane) for the detection of organohalides in water at very low levels (1-0.1  $\mu$ g/1).

Thus, where a unit is challenged with a chloroform concentration of 100  $\mu$ g/1 or greater, for 90% removal a concentration of 10  $\mu$ g/1 or less in the effluent would meet the removal requirement. In such cases

- 97 -

routine monitoring of samples for 10  $\mu$ g/l of the contaminant should be performed by direct aqueous injection. Spot checking by the sparging technique of Bellar and Lichtenberg for determination of actual concentrations, if lower than the detectable levels for the other methods, could be performed.

Liquid extraction - the common terminology for extraction of an aqueous sample with an organic solvent - is the oldest and most widely used technique for extracting organics from water. It is fairly comprehensive in approach, the extraction efficiency being generally acceptable for water insoluble organics of a wide range of molecular weights. Liquid extraction is the method of choice for chlorinated pesticides and chlorinated phenols followed by GC analysis using electron capture detection.

Any analyses undertaken should follow methods listed in the most recent publication of the Federal Register Guidelines establishing test procedures for analysis of pollutants. The guidelines include selected methods from the following: "Standard Methods for the Examination of Water and Waste Water," American Public Health Association; "Annual Book of Standards," American Society for Testing and Materials; "Methods for Chemical Analysis of Water and Wastes," Environmental Protection Agency.

Guidance in interpreting removal results for specific organics should be as follows:

- (i) 90%-100% removal to be considered effective.
- (ii) 10%-90% removal to be considered failing, but still having some degree of effectiveness.
- (iii) 0%-10% to be considered completely failing.

## 12.4 Addendum

A limited number of experiments were performed on purchased units to test their capability for specific chemical removal, viz., Dieldrin and chloroform.

Units purchased were coded. The unit coded Clea (bacteriostatic) contained silver/carbon and Clea (regular) was a similar unit containing only activated carbon. Spra (old) was a unit which had been in daily use for approximately 5 months in the household of a staff member of the ORF.

New units were pre-conditioned according to the manufacturers' instructions prior to testing. An all glass reservoir (30 litre capacity) was used in the tests. Approximately 26 litres of tap water was added to the reservoir and spiked with the chemicals listed above. Samples were removed from the reservoir for initial and final concentration determinations of the spiked chemicals. The spiked water from the reservoir was passed through the test unit at a rate of 2 litres/min under on/off running conditions (5 min on followed by 5 min off) until 25 litres had passed through the unit. Effluent samples were taken at various periods during the program and analysed for the presence of chemicals that had been spiked in the reservoir. The complete above procedure was repeated as required with additional reservoir batches containing 26 litres of spiked water.

The results obtained are presented in the accompanying table. Although, in general, chloroform was removed to a greater extent than Dieldrin, there are marked differences in removal efficiencies depending on the size of the carbon bed and construction of the units. The results shown are intended only as an illustration as to what might be expected in tests run with "spiked" water. Much more testing would be required to obtain definitive efficacy data on the various units.

- 99 -

### Table 1

Unit	Reservoir *			Effluent			% Removal	
Code	Volume (litres)	CHC13	Dieldrin	Volume (litres)	CHC13	Dieldrin	CHC13	Dieldrin
Cera	25	174	49	25	81	27	53	44.8
	50	167	58	50	100	32	40	44.8
	75	154	71	75	107	35	30.5	50.7
Clea (Bacter static	25	240	-	25	2	-	99	-
	$\frac{10}{50}$	230	-	50	2	· · · -	99	-
	75	213	70	75	2	4.9	99	93
	100	270	63	100	2	9.9	99	84
Clea (Regula	25 (r)	250	52	25	2	2.8	99	95
Spra (New)	25	220	71	25	24	37	89	47.8
Spra (01d)	25	250	73	25	22	. 36	91	50.6
ļ								

## ORGANICS REMOVAL (µg/1)

\* The following procedure is recommended for the preparation of spike solutions of the test compounds. Known weights of the test compounds in volumetric flasks are diluted by making up to the mark with either acetone or 95% ethanol in order to prepare stock solutions. Secondary dilutions are performed with the original stock solution using either 50% acetone or 50% ethanol. The appropriate final dilution is made by transferring 1 ml or less of the diluted stock standard to the reservoir with vigorous stirring. Stirring of the reservoir is maintained throughout the duration of the test.

- 1. Bellar, T.A. & Lichtenberg, J.J. The Determination of Volatile Organic Compounds at the µg/1 Level in Water by Gas Chromatography. US EPA, National Environmental Research Center, Cincinnati, Ohio, EPA-670/4-74-009, Nov. 1974.
- 2. Bellar, T.A. & Lichtenberg, J.J. Determining Volatile Organics at the  $\mu$ g/l Level in Water by Gas Chromatography. Jour. AWWA, <u>66</u>, 739 (Dec. 1974).
- Nicholson, A.A. & Meresz, O. Bulletin of Environmental Contamination and Toxicology. 14, 453 (1975).
- 4. Mieure, James P. J. AWWA, <u>69</u>, 60 (1977).
- 5. Richard, J.J. & Junk, G.A. J. AWWA, <u>69</u>, 62 (1977).

. .

TRACE METALS
. . . .

#### TRACE METALS

### Introduction

Consideration of testing protocol of household water treatment units for their trace metal removing capabilities includes the need to monitor the release of silver by those units identified as bacteriostatic.

Trace metal removal claims do not appear on any of the units examined in our laboratory as part of this study which are based on activated carbon and/or ceramic filters. However, such claims could be made for units using reverse osmosis, distillation or deionization (demineralization) as part of the treatment process.

Ideally, testing standards for a specific metal should be selected so as to challenge an individual unit with the equivalent of the "poorest" household water supply with respect to that metal. This selection is complicated by the lack of readily accessible data on the levels of the more toxic metals in drinking water supplies across Canada. Some information is available (1) which shows that the average levels of most metals of concern are generally much less than the maximum concentration limits (MCL) specified by Federal (2) and Provincial regulatory agencies. However, the extreme situations are not identified.

The presence of silver in the bacteriostatic type of filter means that treated water from these units may actually be poorer with respect to silver concentration than the untreated water. The role of silver in these units is considered to be the inhibition of growth of microorganisms on the filter support. Therefore, it is desirable that these units should not release silver into the water. In tests undertaken in our laboratory (Table I) certain of these bacteriostatic type units significantly increased the silver concentration of the treated water above the level in the tap water used, i.e. routinely <0.5  $\mu$ g/ $\ell$  silver in Mississauga water supply. Silver levels in excess of 10  $\mu$ g/ $\ell$  are not a common occurrence (1). In a survey of U.S. municipal water supplies, the range of silver concentrations was 0-2  $\mu$ g/ $\ell$  with a mean of 0.13  $\mu$ g/ $\ell$  (3).

Silver is not considered highly toxic. Argyria, the pigmentation problem, is the major known health concern, although some physiological effects have been reported in test animals receiving higher concentrations  $(>400 \ \mu g/l)$  of silver in their drinking water (4,5). It appears that bacteriostatic water treatment units by increasing the silver concentration in drinking water are introducing a hitherto unknown factor, i.e. the effect on humans of chronic intake of low concentrations of ionic silver. The current MCL is 50  $\mu g/\ell$ . However, it has been reported to us (personal communication) that the European Economic Community Water Quality Standards Committee is proposing to reduce the MCL in the member countries to 10  $\mu g/\ell$ . The reasons behind such a move are not known, but in light of the considered accumulative and irreversible nature of silver adsorption and the potential of increased silver concentrations in treated drinking water, further review is recommended. It would appear that much of the toxicological assessment of silver is based on data derived from the therapeutic use of silver containing formulations or argyria resulting from occupational exposure, i.e. adsorption through skin, lungs or other tissues rather than by ingestion.

The selection of test protocol for trace metals removal and silver release requires consideration of several factors: (a) Test Water, (b) Spike Levels, (c) Operational Procedures, (d) Sample Collection, Preservation and Analytical Techniques, (e) Evaluation of Data and Specifications.

(a) Test Water

Interim requirements for registration of Bacteriostatic Water Treatment Units for Home Use in the Federal Register (6) state that a tap water should be used which approximates to the quality parameters of the tap water at the EPA Laboratory, Beltsville, Maryland. A satisfactory region would be:

pH - 6-8
Hardness as CaCO<sub>3</sub> - 25 mg/l (ppm)
Alkalinity as CaCO<sub>3</sub> - 20 mg/l (ppm)
Total dissolved solids - 10-40 mg/l (ppm)
Temperature - 20-25°C

If such quality tap water is not available, water that has been artificially constituted to the concentration ranges shown, may be used.

In its interim draft #4 covering voluntary standard for portable, household and commercial units, the Water Quality Improvement Standards and Certification Council (7) proposes that each unit should be tested with three tap waters, namely a general test water (TDS 200-600 mg/ $\ell$ ), a low TDS test water (TDS <100 mg/ $\ell$ ), and a high TDS water (TDS >800 mg/ $\ell$ ). Other constituents are described elsewhere in the section of this report on microbiological testing. The tap water should be a regular chlorinated municipal supply.

The low TDS water will be important with respect to potential silver release, whilst the high TDS will affect significantly the lifetime of units utilizing any form of chemical deionization. The EPA test uses the lower TDS water and it would seem more feasible to select a low TDS value of <50 mg/ $\ell$ .

### (b) Spike Levels

EPA preliminary requirements (6) only state that the unit must remove the specified elements throughout the stated life of the filter, but no degree of challenge is suggested. The WQISCC (7) recommends that if an MCL has been established by EPA, the unit should be capable of reducing the concentration of the specific metal from 20X MCL to less than the MCL. Where no MCL exists, the unit should reduce the concentration of the specific metal from 500  $\mu g/\ell$  (ppb) to not more than 25  $\mu g/\ell$  (ppb).

Considering the typical levels found in household water supplies (1), to require a unit to reduce the concentration of a metal by a factor of 20X MCL to less than the MCL (hereafter referred to as the reduction factor) seems impractical. This is particularly true of those metals with MCL values >0.25 mg/ $\ell$ , e.g copper, zinc, etc. We recommend that the reduction factor should not exceed 10X MCL and in the case of those metals with an MCL >0.25 mg/ $\ell$ , a lower factor be used. If no MCL has been established for an element by regulatory agencies, the unit should only

be challenged with that element when the manufacturer claims its removal by the unit. The manufacturer should be able to state and substantiate the degree of removal throughout the life time of the unit.

Mercury is a special situation. The very low levels  $(<l \mu g/l)$ coupled with the very poor stability in neutral aqueous solutions of mercury ion concentrations of 10  $\mu g/l$  (due to adsorption of mercury on to surfaces of containers and tubing, etc.) advise the need for caution in specifying standards and testing units for mercury removal. Conditioning of all apparatus with a mercury solution of higher concentration may prove beneficial but this hypothesis would require careful experimental evaluation.

If the MCL values for other more toxic elements were to be lowered, this type of problem could become more significant.

### (c) Operational Procedure

The operation of the test should simulate as closely as possible the normal recommended operating conditions. Factors such as the number of units tested, etc. should be the same as for microbiological and organics removal testing. In the test protocol, the input water should be tested at regular intervals.

# (d) Sample Collection, Preservation and Analytical Techniques

It is desirable that all analytical techniques be able to accurately measure element concentrations in the ranges expected. Most concern will relate to measurement of element concentrations close to MCL values. Atomic absorption spectrophotometry (AAS) should be the recommended technique and it offers the capability of measuring all trace metals of interest. Lower concentrations (i.e. below flame AAS detection limits) can be measured by either the use of concentration techniques (evaporation, chelation/ solvent extraction) prior to flame AAS analysis or the use of the flameless (graphite furnace) atomization attachments. Anodic stripping voltammetry (ASV) using a hanging mercury drop or mercury film electrode also offers the desired sensitivity for the analysis of a few selected elements, e.g. zinc, cadmium, lead and copper.

If disagreement should arise regarding the validity of test results, the most probable areas of concern would relate to factors such

as cleaning procedures for sample containers, type of container (polyethylene, glass, polypropylene, etc.), preservation procedures, blank reagent values, processing procedures (if any) and interferences during analysis. The last of these factors can be most readily eliminated or identified by the use of techniques such as standard additions during analysis. Thus in our own laboratory we have identified significant enhancement ( $\sim$ 60%) of the response for chromium in acidified Mississauga tap water compared to acidified deionized water standards when analyzed by flameless AAS. In the flame mode the interference using air/acetylene was  $\sim 10\%$  depression of absorbance for chromium. For several elements the MCL values are at or just above the typical "detection limits" quoted for different makes of atomic absorption spectrophotometer. However, close to detection limits the combined electronic and flame noise becomes significant and the accuracy and precision of analytical data measured at these ranges must be considered poorer. All models of AA spectrophotometers offer simultaneous background correction capability. This is considered essential for flameless AAS and may also be considered necessary for the analysis by flame AAS of solutions with higher TDS values. However, the benefit gained from simultaneous correction of non-specific background "absorbance" may be offset by an increased noise level since two sources are now being compared. Therefore, a poorer detection limit will result.

The other factors (container, preservation, etc.) unfortunately represent an area of considerable controversy (8-10). This is particularly true in the analysis of trace concentrations of silver, otherwise such factors are only considered significant in the analysis of those elements with MCL values less than 0.10 mg/ $\ell$ , e.g. lead, cadmium and mercury etc., where adsorption or desorption from container walls could influence values.

It is therefore essential that all analytical and sampling procedures should be approved by the examining agency prior to work being undertaken with the recognition that such approval does not infer automatic acceptance of analytical data.

The analysis of silver warrants specific attention. Using a Varian Techtron AA6 spectrophotometer without background correction and an air/acetylene flame, we can readily detect the current MCL of 50  $\mu$ g/ $\pounds$ (ppb) (cf. Figure 1) using silver standards in 1% v/v nitric acid. However, the noise level is significant and close to the detection limit of 12  $\mu$ g/ $\ell$ , we would question the accuracy of such data. (Varian quotes a detection limit of 3  $\mu g/\ell$  but we have not achieved that figure.) Flameless AAS (Varian Techtron Model 63 or Model 90 Carbon Rod Atomizers) offers a detection limit below 0.1  $\mu g/\ell$ . In our tests included as part of this study, we did not use scale expansion to take us to that level of detection but such a detection limit could be readily achieved. Of concern to us was the observation of multiple peaks in the flameless AAS analysis of silver in Mississauga tap water (Figure 2). This speciation effect was not overcome by passage of the water through any of the filter units tested (inorganic complexes?) and it was impossible to accurately quantitate the silver concentrations. At the current MCL of 50  $\mu g/\ell$ , flameless AAS is not required and therefore such interferences are not critical. If the MCL value for silver was reduced to 10-20  $\mu g/\ell$  (ppb), problems of this nature would be important. Additionally, modern spectrophotometers offer the option of faster electronic systems to allow more accurate measurement of the rapidly generated signals in flameless AAS. However, these systems measure the maximum signal observed during the atomization period and where multiple peaks are present only the largest signal will be reported. If an operator was using flameless AAS in this peak mode to measure concentrations close to the MCL value and he or she was unaware of the multiple peak effect, significant errors would result. Our own tests have only involved Mississauga tap water and we do not know if this interference is a widespread effect. However, a greater in depth study of the analytical chemistry of low concentrations of silver might be warranted.

With another type of filter (not tested in this study) we encountered the problem of silver present as particulates in effluent samples. These particulates were dense and settled rapidly in containers. Quantitation was not possible by flameless AAS due to the small volumes (2.5  $\mu$ ) being sampled for analysis. The possibility of silver particulates being present in solutions in significant quantities is considered slight but cannot be ignored due to the low solubility of many silver salts. A settling test may be advisable to check solutions for this possibility. This could also check for any situation which might result in the release of silver/carbon fines.

Sample collection, preservation and cleaning of apparatus are particularly of concern in the analysis of silver. The literature contains contradictory viewpoints and experimental data (8-14). It is recognized that long term (>10 days) storage of silver solutions is a problem, but using a typical preservation procedure, e.g. acidification to 1% (v/v) with nitric acid, solutions should be sufficiently stable to be analyzed within a period of less than 72 hours. In our own laboratory, using polypropylene apparatus, a cleaning procedure of dilute ammonium hydroxide, conc. HNO<sub>3</sub> and 10% v/v HNO<sub>3</sub>, and rinses with high purity deionized water, we have found that silver standard solutions in 1% v/v nitric acid (deionized water) do not decrease significantly (i.e. >10%) after 72 hours storage at room temperature. Provided apparatus has been cleaned properly, the prime concern is the delay between collection and analysis.

### (e) Evaluation of Data

The EPA interim requirements (6) require that a specific metal be removed for the stated lifetime of the filter. The test involves only challenging of the unit at selected intervals in the lifetime.

We recommend that a continuous challenge throughout the stated lifetime of the unit would be less complicated, particularly if an accelerated test is being used (cf. Organics Removal Section).

Any unit should be able to reduce by the appropriate factor, the metals (specified individually) to below the current individual MCL throughout the stated lifetime of the unit. The silver concentration in the effluent should never exceed the current MCL value. In our tests (Table I) run concurrently with the Organics Removal Tests of selected bacteriostatic units, we identified a trend towards increased silver release (as high as  $26 \ \mu g/\ell$ ) with the progressive volume of effluent collected from two units (Cera and Clea). It is thought that these trends reflect the presence of activated carbon (without silver) in the latter stages of the flow path and as this becomes saturated with silver, the silver concentration in the effluent increases. If this effect is true, accelerated tests using smaller volumes would not give accurate data for the lifetime of the filter unit. It would appear important that the unit is challenged with sufficient water to allow silver concentrations in the effluent to stabilize.

### 13.1 Recommended Test Protocol for Trace Metals

#### (1) Procedure

The recommended operational procedures described in the section on organics removal should also apply to these tests.

### (2) Spiking

Standard chemicals are to be spiked into tap water at concentrations relative to the individual MCL values (if established). It is recommended that where the MCL is 0.25 mg/l or less (i.e. the more toxic metals) the spike level should be 10X the MCL. At MCL values greater than 0.25 mg/l the units shall be challenged with a concentration of 2-3X the MCL. The salts used to prepare spike solutions should be chosen to correspond as closely as possible to the normal anionic species expected to be found in natural water supplies and the concentration of one anion should not be selectively altered, i.e. use mixtures of sulphate, nitrate, chloride, etc.

The tests should be undertaken with not only a regular tap water, but also a low total dissolved solids water (TDS <50 mg/l) and also a high TDS water (TDS >800 mg/l). The low and high TDS samples may be prepared by appropriate treatment of the tap water. The high TDS may be achieved by tap water spiked with sodium carbonate, calcium chloride and/or magnesium sulphate in typical natural preparations. Other parameters, e.g. pH, temp. etc. would be as recommended for microbiological testing.

Metals claimed as being removed shall be specified by manufacturers and tested accordingly. The unit must demonstrate the ability to reduce the metal concentration in the effluent below the MCL value for the stated liftime of the unit. A percentage of lifetime figure may be used in the case of accelerated tests using the high TDS tap water, i.e. the extreme case.

As in the case of organics removal tests, samples of effluent should be collected at the start (immediately after flushing), 25%, 50%, 75% and 100% of the anticipated lifetime of the unit. The feed solution should be sampled at regular intervals depending on the length of the test run.

All samples shall be preserved according to accepted procedures, e.g. acidification to 1% (v/v)  $HNO_3$  for metal analyses. Initial and final effluent samples should be analyzed additionally for pH, calcium, magnesium, sodium chloride, sulphate and total hardness.

A silver release test should also be performed with a unit which has been allowed to age for at least three months. This will be to test for any indication of breakdown of silver deposits due to residues of ammonia in the bed.

#### (3) Analytical Procedure

All analytical procedures should concord with those listed in the current edition of Standard Methods of Water and Waste Analysis. Alternative procedures may be used provided they are acceptable to the examining agency. The same would also be true of situations not covered by Standard Methods. All metal analyses should be performed within a

- 110 -

reasonable time interval from collection, i.e. of preferably less than 48 hours and not more than 72 hours in the case of low MCL metals, e.g. cadmium, silver, mercury, lead, etc.

Atomic absorption spectrophotometry using flame or flameless atomization [graphite furnace, cold vapour (mercury) or hydride generation (arsenic, antimony, selenium)] is the recommended technique. All standards should be prepared in unspiked tap water, unless natural levels introduce analytical problems.

All sampling materials, cleaning procedures, preservation methods and intended analytical procedures, should be submitted to the examining agency for approval prior to undertaking tests, with the understanding such approval does not assume automatic acceptance of these procedures when data are being evaluated.

The silver analysis should include a test based on shaking and immediate aspiration or injection into the AAS, followed by a settling time of five minutes and a second sampling from the same depth in the same bottle, i.e. a test for particulate silver.

# 13.2 Other Recommendations

(1) The use of bacteriostatic filters introduces factors hitherto not considered important, i.e. the level of silver in treated effluents. In our tests the highest detected concentration was 26  $\mu$ g/ $\ell$  and as indicated in the text, the concentration released appeared to be increasing. These tests were performed with regular tap water which is relatively hard (total hardness as CaCO<sub>3</sub>  $\sim$ 140 mg/ $\ell$ ) and has a TDS of 200-250 mg/ $\ell$ . There is need for further study of the effect of these and other factors on the release of silver from such units.

(2) Although not considered of major concern, it is recommended that the toxicology of silver be reviewed, e.g. is there any risk from the formation of inorganic compounds of known or suspected carcogenicity, e.g. silver salts of chromate, dichromate, selenate, selenite, etc.? (3) It is our understanding that the silver in the bacteriostatic filters is deposited by a mechanism similar to the formation of silver mirrors. If the prepared material is not washed adequately, residues of ammonia may lead, on storage, to breakdown of the deposit and release of higher concentrations of silver. This requires further examination and may also have bearing on the shelf life of the units.

(4) With the selected units examined in our laboratory, there are no clear statements of the usable lifetime of the individual unit, i.e. no guide for the consumer. The manufacturer should as a minimal requirement advise the consumer of the usable life of the unit, e.g. relative to the TDS and hardness of the local water supply. There is also need for a simple but sensitive test procedure to allow a user to check that the silver release is not excessive.

(5) A portable type of purifier (Port in Table I) was also tested. This unit is not thought to contain any silver but the significant quantity of fines (carbon) released on the initial flushing could give cause for concern if attempts were made to include silver in the unit. The presence of silver in any type of unit which might be subject to transportation, e.g. campers, mobile homes, introduces the question of the risk of vibration causing the release of carbon/silver fine particles.

# 13.3 Addendum

In the 1976 Annual Report on Water Quality Objectives (15) prepared for the Great Lakes Water Quality Board and Research Advisory Board, it is proposed that the concentration of total silver in an unfiltered water supply should not exceed 0.1  $\mu$ g/ $\ell$  in order to protect aquatic life. This report also mentions the limited data available on the mammalian toxicity of silver, although reference is made to a review of human health aspects (16).

### Trace Metals References

- L.C. Neri, D. Hewitt, G.B. Schrieber, T.W. Anderson, J.S. Mandel and A. Zdrojewsky. J. Amer. Water Works Assoc. (1975) 67,403.
- 2. Canadian Drinking Water Standards and Objectives. Dept. of National Health & Welfare 1968.
- 3. F.B. Taylor. J. Amer. Water Works Assoc. (1963) 55, 619.
- 4. G.D. Barkov and L.I. El'Piner. Gig. Sanit. (1968) <u>33</u>,16. [Chemical Abstracts (1968) 69,54228y]
- 5. Appendix 1962, U.S. Public Health Service Drinking Water Standards. U.S. Public Health Service, Washington, D.C.
- 6. Federal Register (1976) 41, 32778.
- 7. Water Quality Improvement Standards and Certification Council. Voluntary industry standards for portable, household and commercial units for treating water for human consumption. Interim Draft #4 (1977).
- 8. A.W. Struempler. Anal. Chem. (1973) 45, 2251.
- 9. G.G. Eicholz, A.E. Nagel and R.B. Hughes. Anal. Chem. (1965) 37, 863.
- A. Rattonetti. Accuracy in Trace Analysis (P.D. LaFleur, Editor) N.B.S. Special Publication #422 (1976), 633.
- 11. C.W. Chambers and C.M. Proctor. Robert A. Taft Sanitary Engineering Centre Technical Report W60-4 (1960), 4.
- 12. F.W. West, P.W. West and F.A. Iddings. Anal. Chem. (1966) <u>38</u>, 1566.
- 13. F.W. West, P.W. West and F.A. Iddings. Anal. Chem. Acta (1967) <u>37</u>, 112.
- 14. W. Dyck. Anal. Chem. (1968) 40, 454.
- 15. Annual Report on Water Quality Objectives, (1976) p. 28. Great Lakes Water Quality Board and Research Advisory Board, International Joint Commission.
- 16. B.L. Carson and I.C. Smith. Technical Report #3 (1975). Midwest Research Institute, Kansas City, Missouri.

# Trace Metals - Table I

# <u>Concentration of Silver in Effluents</u> <u>From Bacteriostatic Units</u>

Unit* Code	Effluent Volume (l)	Silver Concentration (ppb)	
		Flame AAS	Flameless AAS**
Mississauga Tap Water	Reservoir		<0.5
Cera	0 (after initial flush) 25	17 21	∿12
	50	21	
	75	26	
Clea (Bacteriostatic)	0	<12	∿2
	25	<12	∿6
	50	<12	∿8
	75	20	∿18
	100	14	∿10
Spra (New)	0		∿3
	25		∿1
Spra (Old)	0 25		<0.5 <0.5
Port			<0.5

\* cf. Organics Removal Tests

\*\* Multiple peaks were noticed in all flameless AAS analyses. Values in this column are estimates.



Typical tracing for analysis of low concentrations of silver by flame AAS. Parameters

Instrumentation:		Varian Techtron A.A.6. Spectrophotometer without simultaneous background correction.		
Lamp Current :	:	3 mA		
Wavelength :	:	328.1 nm		
Slit Width :	:	1.7 Å		
Mode :	:	Absorbance		
Scale :	:	x10		
Flame :	:	Air/Acetylene, oxidising		
Matrix :	:	1% (v/v) HNO <sub>3</sub>		

- 115 -

Figure I



Typical tracing for the analysis of the silver content of acidified Mississauga tap water (1% v/v HNO<sub>3</sub>) using flameless atomization AAS (Varian Techtron, Carbon Rod Atomizer, Model 90) and the method of standard additions. An A.A.6. Spectrophotometer was operated in the absorbance mode with simultaneous background correction (Wavelength - 328.1 nm). A sample volume of 2.5  $\mu$  was used with a scale expansion x2.

·

ASBESTOS FIBRE REMOVAL

、

### ASBESTOS FIBRE REMOVAL

#### Summary

Experiments were carried out on four commercially available water purifiers to establish their effectiveness in asbestos fibre removal, and to give guidance in establishing a suitable test specification for admission of such claims.

Previous specifications by most manufacturers were found to be not relevant to the real situation in potable waters, and a specification is recommended which deals only with fibre lengths normally encountered.

The principal difficulty is in definition of the challenge, since standard dispersions cannot be prepared to an accurate specification. Furthermore, the input and effluent fibre analyses have inherent statistical limitations on their accuracy. Accordingly, the specification recommended takes account of these problems, whilst establishing rigid controls on the challenge and the precision of the analytical results. In principle, for admission of a claim, no more than a 5% transmission of the number of fibres between 0.5  $\mu$ m and 10  $\mu$ m length is recommended, the initial challenge being not less than 50 x 10<sup>6</sup> fibres/litre of chrysotile asbestos.

14.0

#### RECOMMENDED TEST SPECIFICATION

1 Using a challenge aqueous dispersion of chrysotile fibres according to the specifications of item 2, no more than 5% of the number of those fibres having lengths between 0.5 µm and 10 µm should pass through the device when used at the manufacturer's recommended flow rate. The measurements of fibre number shall conform to the specifications of items 3, 4 and 5.

2 The challenge dispersion of chrysotile asbestos fibres shall be such that the distribution of the lengths of fibres between 0.5  $\mu$ m and 10  $\mu$ m in length are contained within the bounds of the logarithmico-normal distributions centred on median lengths 0.5  $\mu$ m and 2.0  $\mu$ m, both distributions having a geometric standard deviation of 2.0. (Shown in Figure 5). The total fibre concentration of the dispersion shall not be less than 50 x 10<sup>6</sup> fibres/litre.

3 Filtration of input and effluent for analysis, and preparation of the filter for electron microscope examination should be performed using the procedure in this document.

4 Fibre counting shall be performed by transmission electron microscopy at a magnification exceeding 20,000. Uniformity of fibre deposition on the electron microscope samples shall be demonstrated at equal or better than the 1% significance level by performance of a chi-squared analysis.

5 The precision of the fibre concentration measurements of both input and effluent shall be such that the 95% confidence interval, calculated assuming random distribution of fibres on the electron microscope samples, does not exceed a factor of three.

14.1

6 The absence of extraneous fibre contamination effects on the measurements shall be demonstrated by analysis of controls.

### INTRODUCTION

Claims have been made concerning the removal of asbestos fibres from potable water by end-use water purifiers. A test protocol is required by which such claims can be substantiated. A number of manufacturers and other organizations have attempted to establish test methods, but these have not in general been relevant to asbestos fibres of dimensions normally encountered in potable water supplies.

The basic technique to establish the filter efficiency is very simple: a known challenge in the form of an aqueous dispersion of asbestos fibres is passed through the filter, and the effluent concentration compared with that of the original suspension. The method of measurement of the asbestos concentrations before and after filtration is where the manufacturers' tests are largely deficient.

Chrysotile asbestos is usually encountered in water supplies as individual fibrils about 40 nm in diameter, and from 100 nm to some micrometres in length. In exceptional cases, these may extend to some hundreds of micrometres in length. Nevertheless, the usual situation is from 100 nm to perhaps 50  $\mu$ m. Typical concentrations encountered may be from zero to 100 x 10<sup>6</sup> fibres/litre. The mass concentration of asbestos in such samples is in the nanograms/litre range. Without identifying their origins, tests described by a number of organizations are as follows.

- (a) The filter is weighed before and after a challenge, consisting of a dispersion of "0.5 micron nominal diameter" asbestos.
   Sizing of fibres was performed using an optical microscope at 100X magnification.
- (b) The filter is weighed before and after a challenge, consisting of "0.2 micron to 100 micron range asbestos fibre" in aqueous dispersion. Particle size was determined by "microscopic grid measurement".

14.2

(c) The filter is challenged by a known dispersion of fibres in the 2-4  $\mu m$  fibre length range at two stages in its life, and both the input and effluent are examined by electron microscopy.

Weighing methods can be immediately rejected, since the challenges used bear little resemblence to the real-life situation. Moreover, such medical opinion as is available indicates that the important parameter is fibre <u>number</u>, rather than mass concentration. On a point of technique, it is also extremely bad practice to measure the small mass of transmitted fibres by subtracting the two nearly equal and large measurements of the filter element weight before and after exposure.

Method (c) is the preferable measurement technique, and this would also be appropriate to measure the proposed standard of the Water Quality Improvements Standards and Certification Council. (i.e. reduction of a fibre concentration of greater than  $10^7$  per litre by at least 95%). However, for legislative purposes, closer definitions are required, since the latter standard does not mention particle size. In addition, aqueous asbestos fibre dispersions are not available as accurate standards for this type of test. It is important that any proposed test retain both practicality and rigidity of definition.

#### **EXPERIMENTAL**

## 1 Filter Testing

The equipment used for the other tests was also used for the asbestos measurements on the in-line filter units. The asbestos suspension used for the tests was taken from Lloyd Lake, Matachewan, Ontario. This concentrated natural suspension is a well characterized stable dispersion, and a measured volume was used to spike approximately 20 l of Mississauga tap water. The diluted dispersion was stirred continuously to ensure homogeneity, and about 3 litres allowed to pass through the filter at a flow rate of approximately 2 l/min. The filtered sample was then taken directly into a polyethylene bottle, and immediately afterwards another sample was withdrawn from a side tube situated as close as possible to the input side of the filter. The rest of the 20 litre volume was then allowed to flow through the filter to waste, and another set of samples was taken during passage of the last 5 litres.

In the case of the portable filter, after conditioning of the filter according to the manufacturer's instructions, three charges of the diluted asbestos suspension were passed through it initially to exchange with the clean water. Samples of the input and output were then taken and transferred to polyethylene bottles.

From two of the filters, samples of the carbon-silver residues flushed through during initial conditioning were collected for examination.

# 2 <u>Sample Analysis</u>

The water samples were analyzed for asbestos using the carbon-coated Nuclepore technique. This technique forms the latter part of the more complex procedure of Glass and Chatfield, <sup>(1)</sup> where destruction of organics by ashing is necessary, and has recently been adopted by the US EPA as an interim procedure. <sup>(2)</sup> The Nuclepore filter consists of a polycarbonate material which is

14.3

soluble in chloroform. This type of filter is unique, in that it consists of a continuous, featureless plastic film, perforated by cylindrical holes of a narrowly defined size range. Figure 1 shows a scanning electron micrograph of a 0.1  $\mu$ m pore size Nuclepore filter. It can be seen that the surface structure of this filter presents no obstacles in the identification of particles on its surface.

Using this technique, a small volume of the water in question is first filtered, after which the filter is dried and carbon coated using a vacuum evaporator. A small square of the coated filter is placed on a 200 mesh copper electron microscope grid, and the filter dissolved away using chloroform. For the dissolution process, the Jaffe washer is used. Figure 2 shows the design of washer used by Kalmus, <sup>(3)</sup> which has proved satisfactory in many fields of application since 1954. It consists of a supporting bridge, made from a rectangular strip of stainless steel wire mesh bent sharply to form an inverted "U". The upper flat surface is covered lengthwise with a paper strip cut from a Whatman filter of slightly smaller width than that of the bridge. The end of the Whatman paper strip is bent downwards so as to touch the floor of the petri dish in which it is placed. Grids are placed in the position illustrated, on the top of which are placed portions of the carbon-coated Nuclepore filter. The lid of the petri dish is then placed in position and the assembly allowed to stand for periods of up to two days, after which the plastic filter medium is completely dissolved, leaving a thin carbon film containing the embedded particulate. This sample is then examined in a transmission electron microscope at a magnification of about 25,000, and all fibres in about 10 grid openings are identified, counted and measured.

### 3 Discussion of Nuclepore Filtration Step

Although no particular problem has been demonstrated when using the Millipore type of membrane filter, filtration is undoubtedly the most critical step in the Nuclepore preparation procedure. Filtration is performed using commercially available 1 inch diameter assemblies, consisting of filter funnels

- 123 -

with a sintered glass frit support, and liquid reservoirs with vertical sides. Using vertical sided reservoirs, the geometry is optimized so as to minimize preferential deposition of particulate as a function of position on the filter. Figure 3 shows an optical micrograph of a Nuclepore filter which has been used to filter a concentrated dispersion of taconite tailings. It can be seen that the deposit is extremely non-uniform, with some areas having little or no deposit at all. It has been found experimentally that in the absence of any precautions this is the type of deposit which may be expected if a Nuclepore filter is used in one of these filtration assemblies. Figure 4 shows a scanning electron micrograph of such a taconite deposit on a Nuclepore filter. It can be seen that significant areas, comparable with that of a 3 mm diameter electron microscope grid, could be extracted from such a filter by direct transfer techniques so as to give a totally unrepresentative idea of the filter loading. A heavy deposit of this type permits the non-uniformities to be recognized. However, at the filter loadings normally used for electron microscope sample preparation, such irregularities would go unnoticed and could easily lead to some of the unsatisfactory inter-laboratory comparisons which have so far been conducted.<sup>(4)</sup> This observation was originally extremely worrying, since the direct transfer techniques of specimen preparation rely on absolute uniformity of particulate material deposit over the active area of the filter.

The principal origin of the non-uniformity is the sintered glass frit used to support the Nuclepore filter during the filtration process. Areas of filter closely contacting the flat ground areas of this frit will permit very little filtration to occur, whereas the open areas will permit efficient filtration. The solution to this problem lies in the use of a backing filter. However, even when a backing filter is used, non-uniformities in the deposit are still found, and these appear to be related to the fact that the Nuclepore filter is basically a hydrophobic material. The manufacturer applies a detergent to the surface of the filter, in order to render it hydrophilic; this process, however, does not appear to be entirely satisfactory in some batches. The plasma asher can be used to render the surfaces of many materials hydrophilic. Some success has been obtained in achieving a more uniform particulate deposit by a pretreatment of the Nuclepore filter in the plasma asher.

It can now be seen that water filtration is not the simple topic it at first appears, if a uniform deposit of material on the filter is required. The problems can be largely overcome by bulk ordering of filters, specified with separators of polypropylene, rather than the usual paper variety to which release agents are sometimes applied. If a backing filter is also used, problems of non-uniformity can be minimized. However, problems still occasionally appear; some possibly caused by the filter clamping arrangements on the commercially available equipment, and some by localized hydrophobic areas on the filters themselves.

From the above discussion, it can be seen that filtration in the case of the Nuclepore is an extremely critical step, and the following instructions must be followed precisely if a uniform deposit is to be obtained. Initially, all equipment must be dry; partial wetting of the backing filter leads to a clogged situation which varies the filtration rate over the area of the filter. The backing filter to be used may be any medium or large pore size Millipore filter; the 0.45  $\mu$ m to 5  $\mu$ m pore sizes have been used satisfactorily. The backing filter is placed onto the glass frit support with the vacuum turned on. The Nuclepore filter, shiny side up, is then placed on top of the backing The suction permits the filters to settle firmly onto their support. filter. If any folds appear in the Nuclepore filter it should be rejected and replaced. The liquid reservoir should then be clamped in position, keeping the vacuum on. The water sample should then be poured directly on to the Nuclepore and allowed to filter. If the reservoir is not large enough to contain the required volume, the additional liquid should be added well before completion of filtration. After filtration, the sides of the funnel should not be rinsed. The Nuclepore filter should then be removed and dried.

- 125 -

#### STATISTICAL TREATMENT OF RESULTS

To ensure precision of the final fibre count, statistical controls must be established on the quality of sample preparation.

### 1 Uniformity of Deposit on the Electron Microscope Grids

A check is made using the chi-squared test, to determine whether the number of fibres found on individual grid squares are randomly and uniformly distributed among the grid squares. If the total number of fibres found in k grid squares is n, and the areas of the k individual grid squares are designated  $A_i$  to  $A_k$ , then the total area examined

$$A = \sum_{i=1}^{k} A_{i}$$

The fraction of the total area  $p_i$ , is represented by the individual grid square area =  $A_i/A$ . If the fibres are randomly and uniformly dispersed over the k grid squares counted, the expected number of fibres falling in the region of one grid square with area  $A_i = np_i$ . If the observed number found in that grid square is  $n_i$ , then

$$\chi^2 = \sum_{i=1}^{k} \frac{(n_i - np_i)^2}{np_i}$$

This value is compared with the significance point of the  $\chi^2$  distribution, having (k - 1) degrees of freedom. We may express our reluctance to discard the idea that the deposit is uniform by establishing a very low value of  $\alpha$ , the significance level, and in this work a significance level of  $\alpha$  about 1% would be appropriate. The use of such a small level of significance allows the result to deviate somewhat from uniformity before one is forced to discard the notion that the deposit is uniform.

### 2 The Best Estimate and Confidence Interval of the Fibre Concentration

In the fibre analysis we wish to sample about 10 grid openings from the population of grid openings and determine the mean grid opening fibre count for the population on the basis of our sample. We also wish to determine the interval about the sample mean, which, with a stated degree of confidence, will contain the population mean. This is achieved by calculating the simple arithmetic mean, followed by computation of a confidence interval using the Student "t" distribution. For the two-sided "t" distribution. For the twosided "t" test, n values of grid square fibre count are used. The sample estimate of variance s<sup>2</sup> is first calculated, where

$$s^{2} = \frac{n \sum_{i=1}^{n} X_{i}^{2} - \left(\sum_{i=1}^{n} X_{i}\right)^{2}}{n (n - 1)}$$

If the desired confidence is 100  $(1 - \alpha)$ %, for the two-sided interval the value of t = t<sub>1</sub> -  $\alpha/2$  is obtained for (n - 1) degrees of freedom. For example, if the desired confidence level is 95%, for the two sided interval the value of t<sub>0.975</sub> is obtained for (n - 1) degrees of freedom. If the mean value of fibre concentration is calculated to be  $\overline{X}$ , the upper and lower values of the confidence interval are given by

$$X_{u} = \overline{X} + \frac{ts}{\sqrt{n}}$$
  
and 
$$X_{L} = \overline{X} - \frac{ts}{\sqrt{n}}$$

This confidence interval is the range of values within which, with a stated degree of confidence, the mean value of all grid squares may be expected to lie. It is important to recognize that the chi-squared test and the calculation of the confidence interval are not the same procedure. The chi-squared test is the appropriate test to demonstrate that the fibres are randomly and uniformly distributed on the grid squares selected. A very lossy preparation, for example, which has lost all the fibres from the specimen grid except one, all other grid squares containing no fibres, will give a very low value of chi-squared. This is a statement that those fibres present are very uniformly dispersed, i.e. a nearly constant zero. However, the 95% confidence interval of such a preparation would be very large, indicating an imprecise result.

### 3 Statistical Significance of the Filtration Efficiency Measurements

Using this procedure a one-sided test is used to determine if the mean value for measurements of the input concentration significantly exceeds the mean value for measurements of the effluent concentration.

Initially, the means and sample estimates of variance are calculated for the two techniques. If  $\overline{X}_A$  and  $\overline{X}_B$  are the means for the two techniques and  $s_A^2$  and  $s_B^2$  are the sample estimates of variance for  $n_A$  and  $n_B$  measurements respectively, the estimated variances of  $\overline{X}_A$  and  $\overline{X}_B$  are  $V_A = s_A^2/n_A$  and  $V_B = s_B^2/n_B^2$ .

The effective number of degrees of freedom is f, where

$$f = \frac{\frac{v_A + v_B^2}{v_A^2}}{\frac{v_A^2}{(n_A + 1)} + \frac{v_B^2}{(n_B + 1)}} - 2$$

If the significance level of the test is  $\alpha$ , then the value of  $t_{(1 - \alpha)}$  is obtained for f' degrees of freedom, where f' is the nearest integer to f.

The value of  $u = t_{(1 - \alpha)}$ .  $\sqrt{V_A + V_B}$  is obtained, and this is compared with the difference in the means  $(\overline{X}_A - \overline{X}_B)$ . If  $u > (\overline{X}_A - \overline{X}_B)$  there is no reason to believe that  $\overline{X}_A$  exceeds  $\overline{X}_B$  at the stated level of significance.

#### RESULTS

A summary of the results obtained on the four filter units is shown in Table 1. (Raw data are collected and available to interested parties on request). It is noteworthy that the input concentrations were all attempts to produce the same value, indicating the absolute necessity to sample both input and output <u>close to the filter unit</u>, and also as close as possible in time. The input concentrations after the first measurement were rather more stable, perhaps indicating some initial scavenging of fibres in the pumping equipment.

It can be seen that in all cases there is a lower mean value in the effluent; whether the reduction is significant in terms of the measurement accuracy is another matter.

Table 2 shows the statistical analysis. It can be seen that the CERA unit displayed a definite and high collection efficiency of 98.1%. At 5% significance, however, the two measurements gave conflicting results in the case of the SPRA and CLEA units. This is entirely a consequence of the measurement accuracy, as is the comparative uncertainty of the decision in the case of the PORT unit. The fundamental limitation of accuracy is that of counting statistics; thus any test specification must take account of this fact. It can be seen in Tables 1 and 2 that there were some samples which gave unacceptable variabilities. This could be improved by either repeat electron microscope sample preparation or by further fibre counting. However, the results illustrate the care to be exercised in interpretation of data of this type.

Figure 5 shows the fibre length distribution used to challenge the filter units. It can be seen that there was some variation in size distribution between the tests, particularly in the case of the initial run. However, if a single batch of challenge suspension were prepared to test a group of filters, some of this variability could be eliminated. Such a dispersion can certainly be prepared which has a distribution within the suggested permitted range shown in Figure 5. Examination of the carbon-silver residues which were initially discharged from the filter units indicated that the silver concentrations in these particles were below the detection limit of the equipment (about 0.5%). No further work was performed on this material.

# 14.6 CONCLUSIONS

The experiments show that a viable test for asbestos removal can be established. The features of such a test should include:

- (a) a challenge dispersion similar to that usually encountered;
- (b) reproducibility in the light of the counting statistics limitations;
- (c) input and effluent measurement by fibre counting, rather than mass measurements;
- (d) correct statistical interpretation of the counting data, together with acceptable limits on its variability.

Only one of the filters tested (CERA) would have passed the test specification recommended.

# REFERENCES

- 1. Glass, R.W., and Chatfield, E.J., "Improved Methodology for Determination of Asbestos as a Water Pollutant", Final Report, SZ 02.KL347-4-2073, Science Procurement Branch, DSS Canada.
- 2. E.P.A. Interim Procedure, C.H. Anderson, E.P.A. Athens Laboratory, Georgia.
- 3. Kalmus, E.H., "Preparation of Aerosols for Electron Microscopy", J. Appl. Physics, <u>25</u>, 87, 1954.
- "An Inter-laboratory Study of Asbestiform Mineral Fibre Levels in the Water Supply of Thunder Bay, Ontario". Ontario Ministry of the Environment Report, September 1975.



<u>Fig. 1</u> Scanning Electron Micrograph of 0.1 µm Pore Size Nuclepore Filter Surface




<u>Fig. 3</u> Optical Micrograph of Nuclepore Filter Showing Uneven Deposit of Particulate



<u>Fig. 4</u> SEM Micrograph of Taconite Deposit on Nuclepore Filter, Showing Uneven Deposit of Particulate







TABLE 1

## Summary of Asbestos Fibre Removal Results

# Fibre Concentration Measurements in 10<sup>6</sup> Fibres/litre (Values in Parentheses are ratios of upper to lower 95% confidence limits)

2nd Measurement	Input Concentration Output Concentration	Mean 95% Confidence Interval	18.2 9.9 - 26.5 (2.66)	0.96 0.38 - 1.54 (4.10)*	101.0 29.0 - 173.0 (6.04)*	50.0 27.7 - 72.3 (2.61)	
		95% Confidence Interval	27.5 - 50.5 (1.84)	22.3 - 78.5 (3.52)*	76.0 - 210.0 (2.75)	48.6 - 77.2 (1.59)	
		Mean	39.0	50.4	143.0	62.9	
lst Measurement	Input Concentration Output Concentration	95% Confidence Interval	2.5 - 18.1 (7.08)*	0.70 - 1.46 (2.09)	37.5 - 56.5 (1.50)	30.3 - 39.7 (1.31)	
		Mean	10.3	1.08	47.0	35.0	
		95% Confidence Interval	9.4 - 25.4 (2.70)	46.0 - 69.8 (1.52)	59.5 - 86.1 (1.45)	27.3 - 82.1 (3.01)	
		Input	Mean	17.4	57.9	72.8	54.7
Type of Purifier			SPRA	CERA	CLEA	PORT	

Unacceptably high 95% confidence interval for actual test, this ratio should be lower than a factor of 3. \*

2

TABLE

Asbestos Fibre Removal: Statistical Analyses

1st Measurement 2nd Measurement	Percentage Significance Level Required to Reverse Decision	<0.5	<0.5	10	10
	Removal Demonstrated at 5% Significance?	Yes	Yes *	No *	No
	Measured Fibre Removal, %	53	98.1	29	20
	Percentage Significance Level Required to Reverse Decision	20	<0.5	<0.5	Ŋ
	Removal Demonstrated at 5% Significance?	No <b>*</b>	Yes	Yes	No
	Measured Fibre Removal, %	40	98.1	35	36
	Type of Purifier	SPRA	CERA	CLEA	PORT

95% confidence interval of at least one result exceeds factor of 3. \*

.

.

OTHER PARTICULATE REMOVAL CLAIMS

.

## 15.0 Particulate removal claims (other than asbestos)

A number of water treatment units claim particulate removal and in order to check this function a number of tests may be required.

### Cysts Removal

When tested with a general test water, a low TDS and high TDS water as in the Section dealing with bactericidal and bacteriostatic filters, the unit should reduce the number of 4 to 6  $\mu$ m particles by 3 orders of magnitude, i.e. 99.9%.

### Spore Removal

When tested with a general test water, a low TDS and high TDS water (see Bactericidal Silver Unit Section) the unit should reduce the concentration of 0.4 to 0.6  $\mu$ m particles by three orders of magnitude (99.9%).

### Organic and Inorganic Solids

When tested in waters as above, a synthetic turbidity of not less than 10 turbidity units should be reduced to not more than 1.0 turbidity unit (90% reduction).

AC test dust (AC Spark Plug Division, General Motors) has been suggested as a test simulant for particulate removal but any test material used for challenge should be a characterized material (e.g. ground gypsum) different from the general background dust. The particle size distribution should be defined as detailed in the section on asbestos removal and the same statistical approach should be used, using visual techniques. <u>Acknowledgments</u> The authors would like to thank the officials of the Water Quality Association and members of the WQISCC Technical Committee; Mr. F. Bell (EPA); Dr. V. Armstrong ( NHW, Ottawa); Mr. B.L. Miranda (Ministry of Health, Ontario) and the many manufacturers of water treatment systems and their agents for providing information and helpful discussions during the preparation of this report.